TECHNICAL METHODS

OF

ORE ANALYSIS

FOR

CHEMISTS AND COLLEGES

BY

ALBERT H. LOW, Sc.D.
Formerly Professor of Chemistry, Colorado School of Mines

TENTH EDITION, REVISED
TOTAL ISSUE, FIFTEEN THOUSAND

NEW YORK
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1927

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BY THE SAME AUTHOR

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ALBERT H. LOW

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To My Wife,

Whose encouragement has ever lightened my labors
This Volume is Dedicated

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PREFACE TO THE TENTH EDITION

In this edition the entire work has been carefully revised. Mistakes and typographical errors have been corrected as far as observed. Some omissions have been made and some new subject-matter inserted.

The use of the book in colleges has indicated the advisability of giving some instructions to students who find themselves unprepared to start in with analytical work at once. This requirement is met in the chapter on "Instructions to Students."

The entire aim of the book is to give instructions that will produce good technical results if carefully followed, without embodying too large a mass of alternate methods that are apt to be confusing.

It is hoped that this new edition may more fully merit the favor accorded in the past.

A. H. Low.

Denver, Colorado, September, 1927.

PREFACE TO THE FIRST EDITION

THIS book is primarily intended as an aid to the technical chemist, but it is hoped it may also prove useful to the student desiring to become acquainted with technical methods.

It is a common experience with technical chemists to receive a sample of material with instructions to return the percentage of some constituent whose technical determination is more or less unfamiliar under the given conditions. In such a case the chemist has recourse to his books, and too frequently is quite unable to find a method that is exactly adapted to the material in hand, or that begins at the beginning and tells him just how to proceed. He is thus left to work out his own salvation, possibly at the expense of much valuable time.

In this book an attempt has been made to supply the want thus indicated by describing methods that are adapted to the cases most likely to be met in practice, although it is sometimes practically impossible to devise a short technical method that will meet every probable case.

It has been my aim to make the descriptions so minute and complete that if the operator will follow them exactly he can scarcely fail to obtain satisfactory results. But herein lies a difficulty. There seems to be a tendency among technical chemists *not* to follow directions exactly. In carrying out a method, the alert operator sees a short-cut and takes it, or a "better way" occurs to him and he introduces it in the place of the one given. There would be no ultimate harm in this (since all methods fall short of perfection) if the operator would only take the time to investigate and determine the real value of his ideas. In some cases he might discover that his supposed improvement was spoiling a good method, and he would come to agree with the author of the method who had himself probably gone over the same ground. I have seen methods of my own thus mod-

ified, and ideas hastily adopted whose incorrectness I had previously demonstrated by careful investigation.

I would, therefore, caution operators to accept directions as they stand until they have demonstrated the value of proposed changes to a certainty.

Some of the methods in the following collection have been devised by myself, mainly on the basis of previously well-known facts, some are compilations of the work of others, and some are modifications of existing methods. I have endeavored to give proper credit in all cases.

While I have aimed at correctness, many shortcomings will undoubtedly be found, and I can only hope that, such as it is, my work may prove of some value to those interested. I shall be grateful for any suggestions, or descriptions of improved methods, to be incorporated in a possible future edition.

My thanks are due to Dr. W. F. Hillebrand for valuable information and suggestions.

A. H. Low.

DENVER, COLORADO, May, 1905.

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INSTRUCTIONS TO STUDENTS

WEIGHING

It is assumed that a small portion of a properly dried and mixed sample of powdered ore is issued to each student. My own practice is to issue these portions on small squares of paper, with the instructions to the students to use what they require and return the remainder. At the outset all the students have the same ore.

Mix the sample with the spatula and then spread it out in a thin uniform layer. Usually, 0.5 gram is to be weighed out. See that the balance is in perfect adjustment, so that when the beam is lowered upon the knife-edges the pointer stands at 0 and remains there.

Place the 0.5-gram weight in the left-hand pan. Hold the right-hand pan in the left hand, and, with the spatula, take up small portions of the ore from perhaps a dozen different places on the sample and transfer them to the pan, endeavoring to take about 0.5 gram in all. Now replace the pan on the balance and adjust the weight of ore exactly, removing or adding a little as necessary. Do this by releasing the pans after each adjustment and noting the movement of the pointer, and continue until the pointer finally stands at 0 after lowering, without appreciable movement.

Do not undertake to weigh by noting the relative swings of the pointer. Such a method of weighing is unquestionably exact, but requires too much time. In rapid technical work the swing method is seldom used, as the method described above, wherein the slightest initial movement of the pointer is noted and adjustments quickly made, will result in attaining all necessary accuracy with a great saving of time.

After the correct weight is obtained, gently tap the ore from the pan into the flask or beaker, using the flat side and not the edge of the spatula for tapping, so as not to injure the pan.

Brush in the adhering dust from the pan with a camel's-hair pencil. Do this delicately, using the side of the bristles and not the tips.

In cases where the ore is to be followed by a roughly weighed powdered reagent, the danger of loss is lessened by weighing the reagent on the same pan without first brushing off the adhering ore dust. When the reagent is tapped from the pan it will take most of the ore dust with it, and very little brushing will be necessary. This plan is especially useful when the ore leaves much adhering matter.

With a hygroscopic ore, where the weight changes rapidly on exposure, the above method of open weighing should not be used. The properly dried ore, in sufficient amount, is contained in a small weighing bottle. The weight of the whole is taken, then approximately 0.5 gram of the ore is poured into the receptacle and the weight taken again. When the amount eventually secured is approximately 0.5 gram, this will suffice, as the final result can be easily calculated to the half-gram basis.

FILTRATION

For much of the routine work of technical ore analysis a filter pump is unnecessary; the loop funnel will very satisfactorily take its place. Loop funnels can now be purchased from the supply houses.* About 3 inches in diameter at the top is a convenient size. In filtering, the loop will cause the liquid to form a continuous column in the tube below and the weight of this column will produce a suction in the filter above. A long stem will give a strong suction, but a length of 10–12 cm. is usually sufficient. A platinum cone is not used, as the suction is not strong enough to render it necessary. In order to make the filter fit properly, the second fold is made with one side larger than the other, so that the opened filter will have an angle of something more than 60°. The wet filter will then fit the funnel at the top and be too small below. This will prevent entrance of air and increase the filtering surface, so that slight suction will effect rapid filtration. After the filter has been placed in the funnel, it is held until moistened and then the top is fitted with the finger until it is as air-tight as possible. In working by this method, nothing would be gained by using a funnel having an angle of exactly 60°.

In folding a filter it is a good plan, after the first fold, to tear off about a quarter of an inch from one of the corners. When the com-

* The Denver Fire Clay Co., the Mine & Smelter Supply Co., Denver.

pleted filter is now placed in the funnel and wetted, the torn corner, coming next to the glass, will break the continuity of an air channel that might form along the adjacent fold.

After a filter has been fitted, so that it draws no air, which would indicate a leak, it will sometimes settle down lower in the funnel during the filtration, at the same time forming an opening on the top edge. The open space next the funnel will be V-shaped, and some of the precipitate may get over into the bottom of the V. In this case there need be no loss; the precipitate will not pass the bottom of the V. Do not make the mistake of attempting to close the opening, for as soon as the top is closed the bottom will open, and the precipitate will pass on. All such openings may be closed before beginning the filtration, but not afterward, unless no precipitate has yet gotten over.

Whenever the occasion will permit the use of a porcelain filter plate, it will usually be found much superior to an ordinary folded filter for rapidity of filtration and washing. The filter-plate arrangement is intended to be used with suction, but the loop funnel will provide sufficient suction in most cases, and it has the further advantage that the filtrate can be received in any desired receptacle, without the use of a bell-jar and plate, and transference can thus be avoided. The filter plate, also called a Witt's plate, is made in various sizes. A convenient size for a 3-inch loop funnel has a diameter of about 375 mm. The corresponding paper is a little larger—the size sold as Whatman's No. 2 (4.25 cm.).

To prepare the filtering arrangement, proceed as follows: Center the filter on the plate and wet it. Hold the funnel inverted and raise the plate and filter into place; still holding the arrangement secure, reverse the funnel to its proper position and then set it in its support. Prepare some paper pulp by violently shaking scraps of filter paper in an 8-oz. stoppered flask with about 150 cc. of a hot water. Pour a little of this pulp over the filter. Using an inverted wash-bottle, pour water into the funnel several times, allowing the filter to drain each time, to distribute the paper pulp and fill up any leakages around the edges of the filter.

Asbestos pulp may of course, be substituted for paper pulp, if desired.

The above arrangement can be used to great advantage in many places where the directions in the text call for an ordinary filter.

WASHING A FILTER

I believe it is customary to instruct students to endeavor to keep the wash solution from getting above the top of the filter, in order to avoid loss of precipitate over the edge. My own instructions, based upon the assumption that a loop funnel and a properly fitted filter are used, are just the contrary. *Always* wash above the filter. There will be no loss of precipitate, and the thorough washing of the top of the filter (a most important point) is insured. If the precipitate crawls above the filter, it may all be saved when the filter is removed, by folding over the filter on itself and wiping out the funnel with a twisting motion.

THE BURETTE

Cleaning.—Always see that the burette is clean before use. Mere washing with distilled water is not sufficient. Grease and dirt are likely to accumulate on the inside walls, causing a contained liquid to have an irregular top surface that is difficult to read.

Pour a little cleaning solution * several times through the tube and then wash out with water. The interior of a burette that has been used for permanganate is likely to be lined with a coating of MnO_2. A little strong hydrochloric acid will quickly remove it.

Stopcock.—This should be kept well greased. Remove and dry it, and dry its fitting with a piece of rolled filter paper. Now grease the stopcock with a thin layer of vaseline, or other stiff lubricant, taking care not to obstruct the hole, and replace in the burette.

Filling with Standard Solution.—Unless the burette is absolutely clean and dry, the following procedure should always be carried out: Close the stopcock, shake the standard solution and pour about 2 or 3 inches of the liquid into the burette. Stopper the burette, invert it once or twice and then allow the liquid to run out, either through the tip or the top. Do this at least three times, allowing the burette to drain completely after each washing with the standard solution. After the last draining, fill with the standard solution.

* **Cleaning Solution.**—Dissolve 5 grams of powdered commercial sodium dichromate in 500 cc. of commercial sulphuric acid. The solution may be used cold, but is more effective when warm. It is poured through burettes and into flasks, etc., to remove organic matter and other films.

Position of the Burette.—The burette should be supported in the holder in a position as nearly vertical as possible, in order that the level of the liquid may coincide with the markings on the tube.

Reading the Burette.—Bring the eye on a level with both front and back of the top edges of the liquid and then read the position of the bottom of the meniscus. This avoids parallax and gives all readings from the same relative position. The reading of the exact position of the lower edge of the meniscus is facilitated by placing the finger, or a strip of paper, back of the burette and just touching it, immediately below the meniscus and as close to it as possible. With an opaque liquid, where the bottom of the meniscus cannot be seen, read the top edge, lining the eye on a level with the front and back, as before. A float is often used with opaque liquids, the reading being taken from the mark on the float. A float is very useful if it works perfectly, but it must exactly fit the burette, so as to be always perpendicular and never stick or drag.

Care of the Burette.—It is always best to drain a burette after use and rinse it out with water. Remove the stopcock and then replace it with a small piece of paper between the surfaces, to prevent sticking. Never leave a caustic alkali solution standing in a burette, as it is almost certain to cause the stopcock to stick. If a stopcock sticks, do not try to force it, but go to the instructor for a remedy.

CALIBRATION

For accurate work, the calibration of the measuring apparatus used in the laboratory is a very important matter. Flasks, burettes and pipettes, as ordinarily received from the supply houses, are likely to be more or less incorrect in their markings. Unless the apparatus to be used is known to be correct, or is furnished with corrections, it becomes necessary to calibrate it. For volumetric work it is not really necessary that the apparatus should be absolutely correct, provided the different measures all correspond with each other. It is best, however, while regulating this point, to attain, at the same time, a close approximation to actual correctness.

In determining the true volumes, water is the most convenient substance to employ as a basis of measurement. The United States Bureau of Standards * defines a liter as the volume occupied by a

* Bur. Stand. Cir. 9.

quantity of pure water, at 4° C., having a mass of 1 kg.; the one-thousandth part of the liter, called the milliliter or cubic centimeter, is employed as the unit of capacity.

The temperature of 20° C. is regarded by the Bureau as the standard temperature for glass volumetric apparatus.

The density of pure water at 20° C. is 0.99823; one liter, then, at this temperature, would weigh 998.23 grams in a vacuum. It would weigh less in air, owing to the buoyant effect of the air. One liter of air of 50 per cent humidity, at 750 mm. pressure, weighs 1.19 grams; a liter of water, weighed in air, would therefore weigh 1.19 grams less than in a vacuum. But the brass weights also apparently lose weight in the same way. Taking the density of brass as 8.4, 998.23 grams would occupy the same volume as 118 cc. of water (approximately). The weights would therefore displace 0.118 liter of air. The buoyant effect on the weights is accordingly $0.118 \times 1.19 = 0.14$ gram. The total apparent loss of weight of the water is therefore $1.19 - 0.14 = 1.05$ grams. The apparent weight of the liter of water, then, is $998.23 - 1.05 = 997.18$ grams; accordingly, 1 liter of water, at 20° C., weighed in air with brass weights, apparently weighs 997.18 grams. This makes the weight of the cubic centimeter, under the same conditions, 0.99718 gram. This weight will be taken as the basis of calculation in calibrating the smaller measures.

The above calculation does not take into account certain minor corrections, such as the variations in the weight of air, but the factors considered are sufficient for most purposes.

CALIBRATING A FLASK

Let us suppose we have to calibrate a liter flask. First, weigh the dry flask, then add 997.18 grams to the weights and exactly counterbalance this with recently boiled, distilled water at a temperature of 20° C. Paste a narrow strip of gummed paper around the neck of the flask, so that the upper edge of the strip is on an exact level with the bottom of the meniscus. The paper may be left there, or the mark made permanent by etching, in the usual way, with hydrofluoric acid. Flasks of other sizes may be calibrated similarly. Sufficient water may first be brought to the proper temperature in a second flask, or the weighed water, when of approximately the correct weight, but a little above it, may be brought to 20°, and the weight then adjusted exactly with a small pipette or glass tube.

CALIBRATING A BURETTE

In the case of a burette, the instrument is already graduated and it becomes necessary to determine the correct readings of the graduations. First see that the burette is absolutely clean, although not necessarily dry, then fill it above the mark with recently boiled, distilled water at 20° C. Pour this out and again fill the burette. This is simply to bring the burette to the same temperature as the water. Now bring the bottom of the meniscus to the zero mark. Have ready a small, light, weighed flask of something more than 50-cc. capacity (for a 50-cc. burette). Slowly run 5 cc. of the water in the burette into the flask and take the weight. Note the excess over the first weight; suppose this is 5.01 grams. Now run in more water, to the 10-cc. mark, and weigh again; suppose the excess weight, over that of the flask, is 10.02 grams. Repeat this procedure for every additional 5 cc. of the burette. Suppose the first five weighings of the water were 5.01 grams, 10.02 grams, 15.00 grams, 19.99 grams, and 24.96 grams. These weighings correspond to the 5 cc., 10 cc., 15 cc., 20 cc. and 25 cc. marks on the burette. To find the true volumes at these points, proceed as follows:

One cubic centimeter of water at 20° weighs 0.99718 gram; 5 cc. = 4.985 grams. The actual weight at this point was 5.01 grams. This is 0.03 gram more than it should be; therefore the true reading at the 5-cc. mark is 5.03 cc. (At this point it suffices to call 1 cc. = 1 gram.) At the 10 cc. mark, the weight should be $4.985 \times 2 = 9.97$ grams. It was actually 10.02 grams. This is 0.05 cc. too much, and the true reading is 10.05 cc. Continuing similarly with the other marks, we find the true readings to be 15.05, 19.98 and 24.97.

The above may be thus tabulated:

Burette Mark.	Actual Wt.	Cal. Wt.	True Reading.
5	5.01	4.98	5.03
10	10.02	9.97	10.05
15	15.00	14.95	15.05
20	19.92	19.94	19.98
25	24.89	24.92	24.97

In calculating the true readings, take the difference between the

actual weight and the calculated weight and apply this to the burette reading, according as the actual weight is plus or minus.

Having determined the true readings of the burette at intervals of 5 cc., we may find the intermediate readings by interpolating as accurately as possible. Thus, from the above figures, we may make the table:

Mark	True
1.00	1.00
2.00	2.00
3.00	3.01
4.00	4.02
5.00	5.03
6.00	6.03
7.00	7.03
8.00	8.04
9.00	9.04
10.00	10.05
11.00	11.05
12.00	12.05
13.00	13.05
14.00	14.05
15.00	15 05
16.00	16.04
17.00	17.03
18.00	18.02
19.00	19.00
20.00	19.98
21.00	20.98
22.00	21.98
23.00	22.98
24.00	23.97
25.00	24.97

A second set of columns like the above will complete the table for a 50-cc. burette. Such a table should always be at hand, and should be numbered to correspond with the burette.

In reading a burette, the correction is applied in the following manner: Suppose the actual reading is 18.35. Take the nearest figure of the burette (18.00) and note the correction. In the above table it is +0.02 cc. Apply this to the reading of the burette; thus, 18.35+0.02 = 18.37, the true reading.

CALIBRATING A PIPETTE

Many of the pipettes employed in technical work are used uncalibrated, as, for most purposes, accuracy is not essential. There are some cases, however, in which the necessity for accuracy, or, at least, for a close approximation thereto, requires that the pipette be calibrated. The following method, while not as accurate as the method of weighing, is much simpler and will usually suffice:

Fill the pipette to the mark with distilled water at laboratory temperature, and then allow the water to run into a clean, dry, calibrated flask of the same marked capacity. The exact temperature of the water is immaterial, provided it does not change during the operation, as both flask and pipette are affected in the same ratio by change of volume. Be particular, however, to note the exact method adopted in running the water into the flask—whether the pipette is removed immediately when the main flow ceases, or a certain time is allowed for drainage, and whether or not the drop on the end of the pipette is touched to the neck of the flask—so as to employ exactly the same method in the future. Have a narrow strip of paper pasted vertically across the mark on both the flask and the pipette. Now note the exact level of the water in the flask and make a fine pencil mark on the paper at this point. It may be either above or below the correct mark. (Take all readings at the bottom of the meniscus.) If above, proceed as follows:

With a small glass tube, withdraw the excess water carefully, until the level stands at the correct mark. Now fill the pipette to the mark and then, very carefully, allow just sufficient water to escape into the flask to bring the level once more to the pencil mark. Immediately stopper the tip of the pipette with the finger, hold the pipette vertical, and make a pencil mark on the paper at the water level. This is the correct mark of the pipette. The mark may be made permanent, and may be made to encircle the stem, by etching with hydrofluoric acid in the usual way.

If the pencil mark on the flask comes below the correct mark, proceed as follows: Again fill the pipette to the mark and then allow just enough water to escape into the flask to bring the level of the water therein to the correct position. Stopper the tip of the pipette with the finger and mark the new level of the water on the paper. Now measure an equal distance above the original mark on the pipette

and make a second mark on the paper. This is the correct mark for the pipette.

Before making the mark on the pipette permanent, it is well to check its accuracy by again testing it against the dry flask.

ERROR DUE TO LABORATORY TEMPERATURE

The equivalent of 20° C. is 68° F., and, of course, variations from this temperature of calibration will affect the volumes of solutions. With water, N/10 normal and N/2 normal solutions, the error involved in a variation of 2°, either way is about 0.04 per cent. In a titration where 25 cc. were used, the error would thus be plus or minus 0.01 cc. The small error due to slight changes of temperature from 20° is usually ignored in technical work, but in particular cases it should be allowed for.

TABLE OF CORRECTIONS *

Temperature, Degrees C.	Correction, cc. per Observed Liter to Give Volume at 20°.		
	Water.	N/10 Solutions.	N/2 Solutions.
15	+0.8	+0.8	+1.0
16	+0.6	+0.7	+0.8
17	+0.5	+0.5	+0.6
18	+0.3	+0.4	+0.4
19	+0.2	+0.2	+0.2
21	−0.2	−0.2	−0.2
22	−0.4	−0.4	−0.5
23	−0.6	−0.6	−0.7
24	−0.8	−0.9	−1.0
25	−1.0	−1.1	−1.3

* Mahin's Quantitative Analysis, Bur. Stand. Cir. 19, Table 33.

CALCULATIONS

In making the necessary calculations for volumetric work, I have found that the students' main difficulty is inability to determine the method of attack. There is a failure to recognize the logical steps to be taken to solve the problem.

The following instructions are given in an endeavor to make the logical sequence of the necessary thought as plain as possible.

Question.—What are the logical steps to be taken in determining the necessary strength of a standard solution, so that 1 cc. will equal 1 per cent of a given substance?

First.—Consider what *weight* of substance must be equaled.

Second.—Consider what happens to the active agent in the standard solution during the titration, and in what way the substance titrated is affected. Is the substance titrated the substance to be determined, or is the latter simply one of its constituents, or does the substance titrated simply represent the substance to be determined? In any case, consider carefully just what happens, either immediately before or during the titration, so as to establish a weight relationship between the active titrating agent and the substance to be determined.

A short study of the situation will usually render the writing out of long reactions quite unnecessary.

Third.—Apply the weight relationship found to the weight representing 1 per cent of the substance to be determined, and thus find the weight of active agent that must be in 1 cc. of the standard solution to equal this weight of the substance to be determined.

This establishes the required strength of 1 cc. of the standard solution in grams, and this figure, multiplied by 1000, gives the strength in grams per liter.

EXAMPLE No. 1

Question.—What should be the strength of a standard solution of silver nitrate, in order that 1 cc. may equal 1 per cent of chlorine in a soluble chloride?

First.—What is the *weight* to be equaled? This evidently depends upon the weight of substance taken for analysis. Suppose this is 0.5 gram, then 1 per cent is 0.005 gram. One cubic centimeter of the silver nitrate solution must then be made equal to 0.005 gram of chlorine.

Second.—Silver nitrate is the active agent in the standard solution. What happens to it during the titration, and what happens to the substance titrated, the soluble chloride? A precipitate of insoluble silver chloride is formed, the silver nitrate furnishing the silver, and the soluble chloride the chlorine. The soluble chloride gives up all of its chlorine, which is the substance to be determined. In this case it is simply necessary to establish a weight relationship between the silver nitrate and the chlorine. $AgNO_3$ is changed to AgCl. One molecule of silver nitrate requires 1 atom of chlorine to effect the change. We may therefore say $AgNO_3 = Cl$. To establish the weight relationship, simply insert the atomic weights; 169.89 parts by weight of $AgNO_3 = 35.46$ parts by weight of Cl.

Third.—Apply the weight relationship determined above to the weight representing 1 per cent of chlorine, 0.005 gram. Solve the proportion, $169.89 : 35.46 = x : 0.005$. $x = 0.02396$. This shows that there should be 0.02396 gram of silver nitrate in 1 cc. of the standard solution. Multiplying by 1000, we have 23.96 grams per liter.

EXAMPLE No. 2

Question.—What should be the strength of a potassium permanganate solution in order that 1 cc. may equal 1 per cent of iron, when 0.5 gram of substance is taken for the determination?

First.—What is the *weight* to be equaled? As we start with 0.5 gram of substance taken for analysis, 1 per cent is 0.005 gram. Accordingly, 1 cc. of the permanganate must equal 0.005 gram of iron.

Second.—What happens to the active agent, potassium permanganate, during the titration? The substance titrated is a ferrous salt of iron; the substance to be determined, iron, is one of its constituents. Potassium permanganate is an oxidizing agent and becomes reduced. The Mn in the $KMnO_4$ changes its apparent valence from 7 to 2, and 5 valences, equivalent to $2\frac{1}{2}$ oxygen, are lost. To avoid the fraction, double the molecule and consider that $K_2Mn_2O_8$ loses 5 oxygen; we may

thus say $K_2Mn_2O_8 = O_5$. Next, consider what happens to the ferrous salt; it is oxidized to a ferric salt. It is not necessary to consider any special salt of iron, such as the sulphate or chloride, nor to write out a long reaction. The result will not be changed if we simply consider that FeO is oxidized to Fe_2O_3, as follows: $2FeO + O \rightarrow Fe_2O_3$. This shows that for, every 2Fe one oxygen is required, giving the relation $O = 2Fe$. Now, $K_2Mn_2O_8 = O_5$, and therefore = 10 Fe. To obtain the weight relationship, simply insert the atomic weights; 316.06 parts by weight of $K_2Mn_2O_8 = 558.4$ parts by weight of Fe.

Third.—Apply this weight relationship to 1 per cent of iron. As the weight of substance taken for analysis was 0.5 gram, the weight of 1 per cent is 0.005 gram. The weight relationship therefore gives the proportion $316.06 = 558.4 = x : 0.005$. $x = 0.00283$ gram. This is the weight of $KMnO_4$ that must be in 1 cc. Multiplying by 1000, we have 2.83 grams per liter.

EXAMPLE No. 3

Question.—What should be the (theoretical) strength of a standard solution of sodium thiosulphate, in order that 1 cc. may equal 1 per cent of lead, determined by the chromate method? (Chapter XVI.)

First.—What is the weight of lead to be equaled? Starting with 0.5 gram of substance, this will be 0.005 gram. In this case, then, 1 cc. of the thiosulphate must equal 0.005 gram of lead.

Second.—What happens to the active agent, sodium thiosulphate, during the titration? It reacts with the substance titrated, which is iodine, and not lead or even a compound of lead. In this case the iodine simply represents the lead, a certain amount of iodine representing a definite amount of lead. How does this happen? Immediately before the titration, the lead compound obtained, which is lead chromate, is dissolved in a strong hydrochloric acid mixture which sets free all the chromic acid in the compound. Potassium iodide is then added, and is immediately decomposed by the chromic acid setting free an equivalent amount of iodine. This is the substance titrated. Now let us see what the different relations are. The formula of lead chromate is $PbCrO_4$; from this molecule the hydrochloric acid sets free CrO_3. This allows us to say that every $Pb = CrO_3$. When potassium iodide is now added, the reaction between it and the chromic acid may be written, $CrO_3 + 3KI + 6HCl \rightarrow CrCl_3 +$

$3KCl+3I$. It is not necessary to write out this reaction if we remember that Cr changes its valence from 6 to 3; the 3 valences lost correspond to the iodine set free, or 3I. However figured, we find that CrO_3 corresponds to or equals 3I; then Pb, which equals CrO_3, may be also said to equal 3I. In the titration, then, the amount of iodine that represents lead is determined by the relation $3I=Pb$. The reaction between the thiosulphate and the iodine is $2(Na_2S_2O_3)+2I \rightarrow 2NaI+Na_2S_4O_6$ (sodium tetrathionate). This shows that $2(Na_2S_2O_3)=2I$, or, $Na_2S_2O_3=I$. As $Pb=3I$, it will equal $3(Na_2S_2O_3)$. To establish the weight relationship between the lead and the thiosulphate, insert the atomic weights; 474.36 parts by weight of $Na_2S_2O_3=207.2$ parts by weight of Pb.

Third.—Apply this weight relationship to the weight representing 1 per cent of lead, i.e., 0.005 gram. We have the proportion, $474.36 : 207.2 = x : 0.005$. Before solving this, however, we must remember that crystallized sodium thiosulphate contains water, the formula being $Na_2S_2O_3+5H_2O$. This will change the figure 474.36 to 744.6, and the correct proportion is $744.6 : 207.2 = x : 0.005$. $x=0.01797$ gram, the weight of crystallized sodium thiosulphate theoretically required in 1 cc., or 17.97 grams per liter.

It is explained, in the determination of lead by the chromate method, that this theoretical figure would give a slightly weak solution, producing high results. In actual trial against pure lead, 1 cc. would be found to equal something less than 1 per cent lead, approximately 0.9926 per cent. Therefore, if the theoretical figure, 1 per cent, were used in a lead determination, it would give a slightly high result.

The above examples are perhaps sufficient to indicate the logical steps to be taken to determine the necessary strength of a standard solution to be used for estimating percentage. While the explanations may appear long, the gist of the matter can usually be gotten at very simply, as in the permanganate example above, without writing out long reactions. Of course, a certain amount of previously acquired chemical knowledge is necessary, and without the ability to think carefully and logically, the student will be at a loss in any case. The main point is to learn to think for oneself in a clear, logical manner, coupling this ability with all the chemical knowledge applicable to the case, that one may possess.

PREPARATION OF A STANDARD SOLUTION

After the necessary strength of a standard solution has been determined, the next question is, what are the steps to be taken in actually preparing it? In the first place, is it necessary to have the solution of exactly the theoretical strength, or will an approximately correct solution fully suffice? Usually an approximately correct solution will serve perfectly, provided its exact strength is accurately determined. Such a solution must, of course, be used with a factor, while if it were exactly correct, as 1 cc. = 1 per cent, no factor would be required, and the result could be read directly from the burette. This advantage of a correct solution is usually more than offset by the fact that it will not *stay* correct very long. A re-standardization will show a change, and it will soon become necessary either to carefully readjust the solution by increasing or diminishing its strength, which is a tedious procedure, or to use it in conjunction with a proper factor. The latter is far simpler and will give equally correct results. But if a factor has to be employed soon after making a solution, why take the trouble to make it exactly correct in the first place? This reasoning does not fit every case, but ordinarily an approximately correct solution will be all-sufficient, especially if use is made of a four-place logarithm table mounted on cardboard for rapid reference.

We shall now assume that an approximately correct solution is to be prepared. The usual procedure with a solid will be described.

First.—Weigh out the determined amount for a correct solution. No great accuracy is necessary, but if the substance is likely to be slightly impure, as is potassium permanganate, or to have a variable water content, as in the case of crystallized sodium thiosulphate or potassium ferrocyanide, endeavor to correct for the probable error by weighing out a little more or less, as judgment dictates.

Place the weighed substance in a fairly large beaker, add distilled water of laboratory temperature, stir the mixture for a short time and then pour the clear portion into the clean measuring flask, which

need not be accurately calibrated. Continue adding more water to the undissolved solid, stirring and pouring as before, until it is all dissolved and transferred to the flask. Be careful not to add the water too fast and thus fill the measuring-flask before all the solid is dissolved. Some substances that dissolve very easily, such as silver nitrate, can be dissolved directly in the flask in a limited amount of water. Finally, fill up the flask to the mark, insert the stopper and mix well by repeated inversion and agitation. Now transfer the solution to the bottle in which it is to be kept. The bottle need not be perfectly dry, but should be as dry as it can possibly be made by draining, after it has been cleansed and washed with distilled water. What little water still adheres to the inside will not materially alter the strength of the solution, which is intended to be only approximately correct at best. Again mix well in the bottle.

Second.—Now comes the standardization to determine the exact strength; this may be done in various ways, depending upon the case in hand. In ordinary cases the solution is balanced or standardized against a known amount of something of known purity or reactive value, such as a silver solution against pure sodium chloride, or a permanganate solution against pure iron, or a pure oxalate; or a thiosulphate solution against pure copper, or against a permanganate solution with a known iodine value. In any case, before proceeding to carry out the plan adopted, we must know how much of the standard substance or solution to standardize against; otherwise, the amount taken might result in a very undesirable titration; that is, altogether too much or too little of the solution being standardized might be required to balance this amount. One must decide on the approximate amount of the solution preferably to be used in the titration; while it would be undesirable to use more than a buretteful, 5 or 10 cc. would be too little. For a 50-cc. burette, about 40 cc. would be a convenient amount. Supposing this amount is decided upon, how much of the standard substance or solution should be weighed out or taken, to require about 40 cc. of solution in standardizing?

Reference to some book may give the desired information, but the student should be able to determine it for himself. Proceed as follows: Note the reaction that occurs during the titration and determine relationships as before described, such as that of silver nitrate to sodium chloride, or copper to permanganate solution of known iodine value. A consideration of the first case will serve to illustrate the calculation.

The reaction between silver nitrate and sodium chloride, both in solution, may be written, $AgNO_3+NaCl \rightarrow AgCl+NaNO_3$. One molecule of $AgNO_3$ corresponds to 1 molecule of NaCl, or, for brevity, we may say $AgNO_3=NaCl$. Inserting the atomic weights, we have, 169.89 parts by weight of $AgNO_3=58.46$ parts by weight of NaCl. Now, how much $AgNO_3$ is there in 40 cc. of our solution? If it were made up so that 1 cc. were approximately equal to 1 per cent of chlorine on the half-gram basis, it would contain approximately 23.96 grams per liter, or 0.02396 gram per cubic centimeter. For the purpose of this calculation, we may assume the solution to be of exactly the correct strength, and that 1 cc. contains 0.02396 gram of $AgNO_3$. Forty cubic centimeters will therefore contain 0.9584 gram. From the above relationship we obtain the proportion, $169.89 : 58.46 = 0.9584 : x$. $x=0.3298$ gram. This is the amount of NaCl corresponding to 40 cc. of our solution, and is approximately the amount to weigh out for the titration.

Third.—Having made the titration, calculate the exact strength from the data now at hand. Suppose, for a silver nitrate solution, that 0.3277 gram of NaCl had been weighed out and that 39.1 cc. of solution were required. One cubic centimeter would then be equal to 0.008379 gram of NaCl. To how much chlorine does this correspond? One molecule of NaCl corresponds to 1 atom of Cl, or, we may say, NaCl = Cl. By weight, this is 58.46 NaCl = 35.46 Cl. This gives the proportion, $58.46 : 35.46 = 0.008379 : x$. $x=0.005083$ gram. One cubic centimeter of our solution thus equals 0.005083 gram of chlorine, or 1.0166 per cent on the half-gram basis. In the subsequent use of this solution, on the same basis, the calculation is very quickly performed:

Cc. used, say 26.75; log . .	1.4273
Log. of factor	0.0070
Log. of result	1.4343 = 27.18 per cent Cl.

In the case of silver nitrate, the salt may easily be obtained very pure. A definite predetermined amount may be accurately weighed out; it dissolves quickly in the measuring flask without recourse to a beaker, and, if the measuring flask is accurate, there is no difficulty in preparing a standard solution that need not be checked.

SECONDARY USE OF STANDARD SOLUTIONS

It frequently happens that a standard solution, prepared originally for the determination of some particular substance, may be made to serve satisfactorily in the determination of something else. Of course, when so employed, another factor is necessary, but unless this factor proves to be inconveniently large or small, the procedure is perfectly satisfactory and saves preparing another solution.

When a standard solution can be so employed, it is a good plan, after standardizing, to mark on the bottle label not only the factor for the principal substance, but also the calculated factors for other substances for which it is likely to be used. As an example, suppose a permanganate solution has a certain value for iron, say, 1 cc. = 1 per cent Fe on the half-gram basis. What would be its value for antimony on the same basis?

When iron is oxidized in the permanganate titration it may be considered that FeO is changed to Fe_2O_3, in accordance with the equation $2FeO+O \rightarrow Fe_2O_3$. We may therefore say, for brevity, $O=2Fe$. When antimony is similarly oxidized by permanganate the change may be regarded as from Sb_2O_3 to Sb_2O_5; $Sb_2O_3+O_2 \rightarrow Sb_2O_5$. In this case O_2 corresponds to or equals Sb_2, which is the same ratio as $O=Sb$. Now if $O=2Fe$ and $O=Sb$, then $2Fe=Sb$. Inserting the atomic weights, we have 111.68 parts by weight of $Fe=120.2$ parts by weight of Sb. If 1 cc. of our solution equals 1 per cent Fe, its value for antimony may be found from the proportion, $111.68 : 120.2 = 1 : x$. $x=1.076$ per cent.

What would be the value of the same solution, on the same basis, for CaO, the method being the titration of the oxalate?

Start as before, $O=2Fe$. Now consider what happens to the calcium oxalate obtained in the analysis. Previous to the titration it is mixed with hot, dilute sulphuric acid. This forms calcium sulphate and sets free a corresponding amount of oxalic acid, which is then titrated. The formula of calcium oxalate is CaC_2O_4; this, by the decomposition, gives $H_2C_2O_4$. This is oxidized in the titration as follows: $H_2C_2O_4+O \rightarrow 2CO_2+H_2O$. Using the equality sign as before, we have $CaC_2O_4=H_2C_2O_4=O$. Every CaO corresponds to CaC_2O_4, and we may therefore say, $CaO=O$. If $O=2Fe$, then $2Fe=CaO$, or, $111.68Fe=56.07CaO$. Now form the proportion, $111.68 : 56.07 = 1 : x$. $x=0.5023$ per cent.

As we have determined the factors for Sb and CaO when the percentage value of 1 cc. of the permanganate solution was taken as 1 per cent, these same factors may be used in any other case when the factor for iron is other than 1. Simply multiply the determined factor for Fe by the above factors.

In this way, in similar oxidizing reactions with permanganate, the factors for other substances may be determined.

Consider another case: If 1 cc. of a thiosulphate solution equals 1 per cent copper, on the half-gram basis, what would be its theoretical factor for lead?

In the copper titration we add potassium iodide to a solution of copper acetate, and iodine is set free and titrated. In the lead titration lead chromate is first decomposed with hydrochloric acid and a corresponding amount of chromic acid is set free. Potassium iodide is now added and the chromic acid sets free a corresponding amount of iodine, which is titrated. In each titration a certain amount of iodine corresponds to a certain amount of either copper or lead. What is the relationship between the iodine and the metal in each case? With copper, Cu=I (see Copper Determination). With lead, Pb=3I (see Chromate Method for Lead). This gives the relationship between copper and lead as 3Cu=Pb, or, 190.71 parts by weight of copper equal 207.2 parts by weight of lead. From this, form the proportion, 190.71 : 207.2 = 1 : x. x = 1.086 per cent. This is the theoretical factor for multiplying the copper factor to obtain the lead factor. As previously explained, it cannot be used in practice, owing to certain unavoidable errors in the lead determination. Actual determination of the proper factor with pure lead shows it to be approximately 1.078 times the copper factor.

It is hoped that the above explanations are sufficient to enable the student to make similar calculations for himself.

All such work involves a line of clear, logical thought and a certain amount of chemical knowledge. I have usually found that I was safe in assuming the chemical knowledge, and the burden of effort has been to habituate the student to correct thinking.

NORMAL AND PERCENTAGE SOLUTIONS

A normal solution may be defined as one containing 1 gram-equivalent of the active substance in 1000 cc. The gram-equivalent is that fraction of the molecular weight of the substance, in grams, which corresponds to 1 hydrogen equivalent. Thus, in the case of hydrogen chloride, the gram-equivalent is 36.46 grams, since the entire molecule, HCl, corresponds to 1 hydrogen equivalent. With H_2SO_4, the molecule corresponds to 2 hydrogen equivalents, so that the gram-equivalent is one-half the molecular weight in grams, or 49.038 grams. With $KMnO_4$, in an oxidizing reaction, the apparent valence of the Mn changes from 7 to 2. In this case the molecule corresponds to 5 hydrogen equivalents and the gram-equivalent is one-fifth the molecular weight in grams, or 31.606 grams.

A normal solution is frequently too strong or too weak for convenience, and simple multiples or decimal fractions of the normal strength are then employed, such as twice normal, ordinarily written 2N, or one-tenth normal, written N/10.

The use of a solution based on the normal system is an advantage in certain cases. All such solutions correspond with each other, either directly or in a simple manner; each cubic centimeter corresponds to an amount of the substance titrated that is at once deduced from its atomic or molecular weight. On the other hand, such solutions are troublesome to prepare and are likely to require frequent and tedious readjustment, so that I do not recommend their use except in certain special cases in which they have a distinct advantage.

A percentage solution is one in which 1 cc. equals a percentage of the substance to be determined. The percentage selected for convenience is usually a simple number, such as 1, 2 or 0.5 per cent. It is evident that, in order to correspond with a certain percentage value of the solution, the same amount of substance must always be taken for analysis. In the determinations of ore analysis it is customary to start with 0.5 gram of substance, or some simple multiple of that amount. A percentage solution has the advantage, over a solution based on the normal system, that it will give percentages directly by the use of a simple weight at the start. To obtain percentages with a solution based on the normal system, the calculated weight of substance to be taken is usually not simple and does not permit of rapid manipulation.

Both normal and percentage solutions are equally troublesome to prepare with exactness, and both, of course, are equally susceptible to change. An inexact solution requires either readjustment or the use of a factor. Although there is a difference of opinion on this point, I personally much prefer the use of a factor in connection with the employment of a four-place logarithm table mounted on cardboard. Re-standardization can usually be performed quickly and the proper factor determined. By the use of logarithms, as above, the calculation is very rapid; suppose 15.65 cc. were used, where 1 cc. of the solution equals 1.02 per cent of the substance being determined, instead of exactly 1 per cent. The log of the factor is 0.0086. This figure is retained until the next re-standardization. Calculation:

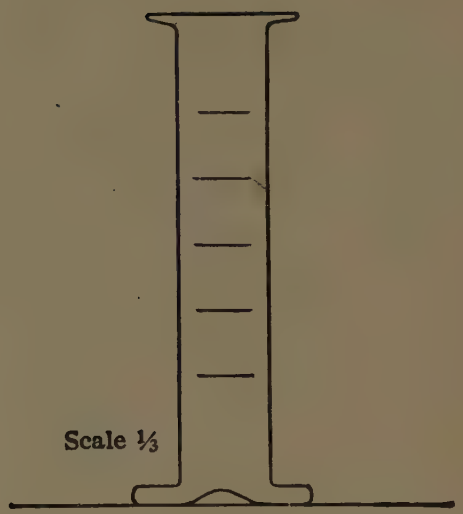
1.1945 (log of 15.65.)
0.0086 (log of factor.)
1.2031 (log of result.) Result = 15.95 per cent.

Where a large number of titrations have to be made with great rapidity, it is perhaps worth while to take the time to readjust a solution to an exact simple value at the outset, but ordinarily this tedious procedure may be advantageously dispensed with, as the results obtained with an accurately standardized, approximately exact solution are equally accurate, and the time required for the calculation is trifling.

In most of the methods described in this book, approximately exact percentage solutions are employed.

Filter plate and filter in loop funnel

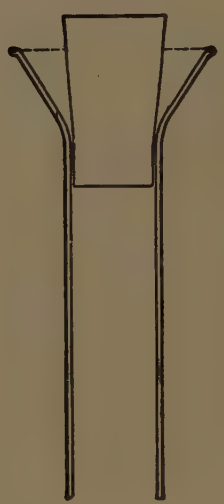
Filter plate



Twenty-five cubic centimeter graduate with thin flanged top instead of lip.

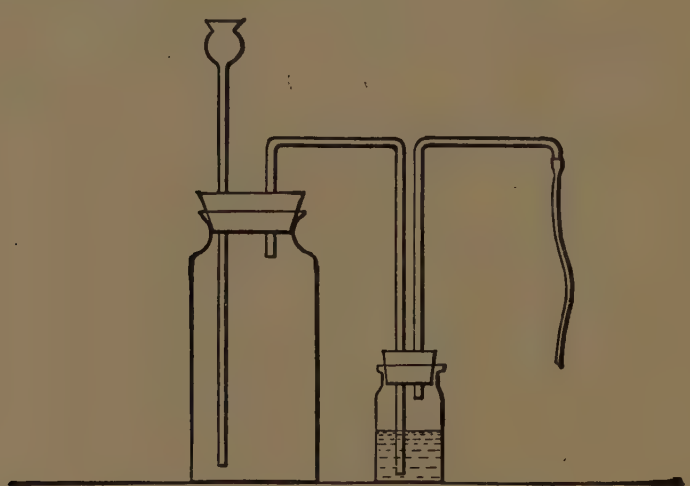
Eight-ounce "Copper flask."

Flask holder.



Top of burette, made funnel-shaped for convenience in filling.

Boiling rod.



Hydrogen sulphide generator.

TECHNICAL METHODS OF ORE ANALYSIS

CHAPTER I

APPARATUS

THE standard works on quantitative analysis give descriptions of the usual apparatus required, and a repetition of the information is not contemplated here. I shall simply mention a few articles and arrangements that I have found convenient in my laboratory.

1. **Flasks.**—For most of my work I formerly used a 6-oz. flat-bottom flask, ordering a special form having a funnel-shaped mouth,

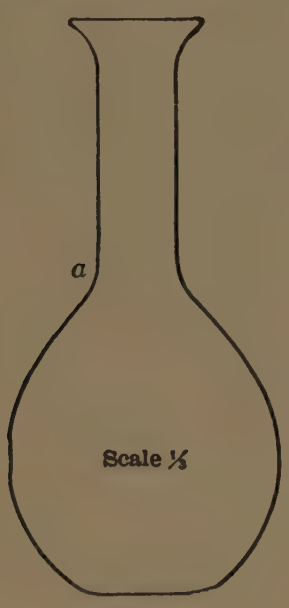


FIG. 1.

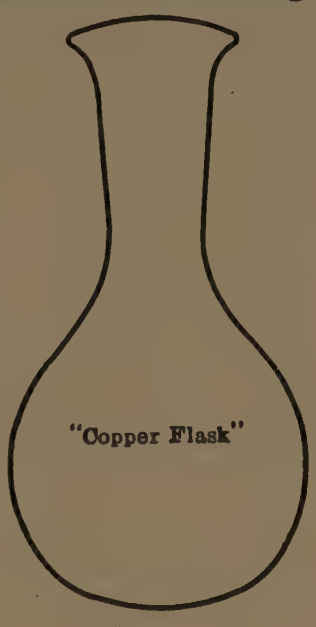


FIG. 2.

FIG. 3.

as shown in Fig. 1. The enlarged mouth was for convenience in pouring and brushing in weighed material from the scale-pan. I subsequently preferred an 8-oz. flask and found those manufactured by the Whitall Tatum Co., of Philadelphia, very suitable. Their shape is shown in Fig. 2. Pyrex flasks of similar size and shape are

now to be obtained and are generally to be preferred on account of their resistance to sudden heat changes. Small Erlenmeyer flasks, with funnel-shaped mouths, as in Fig. 3, are useful in special cases. Five-hundred cubic centimeter Erlenmeyer Pyrex flasks are to be preferred for the zinc determination, as the glass is free from zinc, and will therefore permit the use of hydrofluoric acid in the decomposition, if necessary.

2. Casseroles.—Flasks are generally prescribed throughout this book, instead of casseroles, for decompositions. They appear to be less liable to mechanical losses of their contents, and for accurate work are generally better adapted and more convenient. In smelter laboratories, where many determinations have to be made daily, casseroles, in connection with a large hot plate, are usually preferred. The usual size is about $3\frac{3}{4}$ in. in diameter. In many of the cases where I prescribe flasks for decompositions the operator may employ covered casseroles if he prefers.

3. Funnels.—For ordinary routine work I do not use a filter-pump or 60° Bunsen funnels. I take a cheap funnel of about the dimensions shown in the figure and modify it as follows: Cut off the stem a short distance below the neck and melt on a glass tube provided with a loop as shown. In filtering, the loop will cause the liquid to form a continuous column in the tube below and the weight of this column will produce a suction in the filter above. A long stem will give a strong suction, but a length of 10–12 cm. is usually sufficient.* A platinum cone is not used, as the suction is not strong enough to render it necessary. In order to make the filter fit properly, the second fold is made with one side larger than the other, so that the opened filter will have an angle of something more than 60°. The

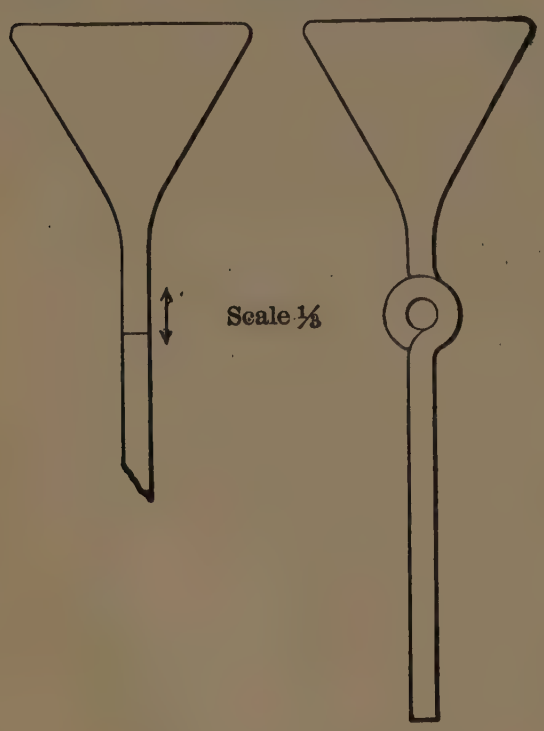


FIG. 4.

* These funnels, and also the other articles mentioned in this chapter, are kept in stock by the Denver Fire Clay Co.

wet filter will then fit the funnel at the top and be too small below. This will prevent entrance of air and increase the filtering surface, so that slight suction will effect rapid filtration. After the filter has been placed in the funnel, it is moistened and the top pushed down and fitted with the finger until it is as air-tight as possible. In working by this method, nothing would be gained by using a funnel having an angle of exactly 60°.

In folding a filter it is a good plan, after the first fold, to tear off about a quarter of an inch from one of the corners. When the completed filter is now placed in the funnel and wetted, the torn corner, coming next to the glass, will break the continuity of an air channel that might form along the adjacent fold.

Whenever the occasion will permit the use of a porcelain filter plate, (Fig. 4*a*), it will usually be found much superior to an ordinary folded filter for rapidity of filtration and washing. The filter-plate arrangement is intended to be used with suction, but the loop funnel will provide sufficient suction in most cases, and it has the further advantage that the filtrate can be received in any desired receptacle, without the use of a bell-jar and plate, and transference can thus be avoided. The filter plate, also called a Witt's plate, is made in various sizes. A convenient size for a 3-inch loop funnel has a diameter of about 375 mm. The corresponding paper is a little larger—the size sold as Whatman's No. 2 (4.25 cm.).

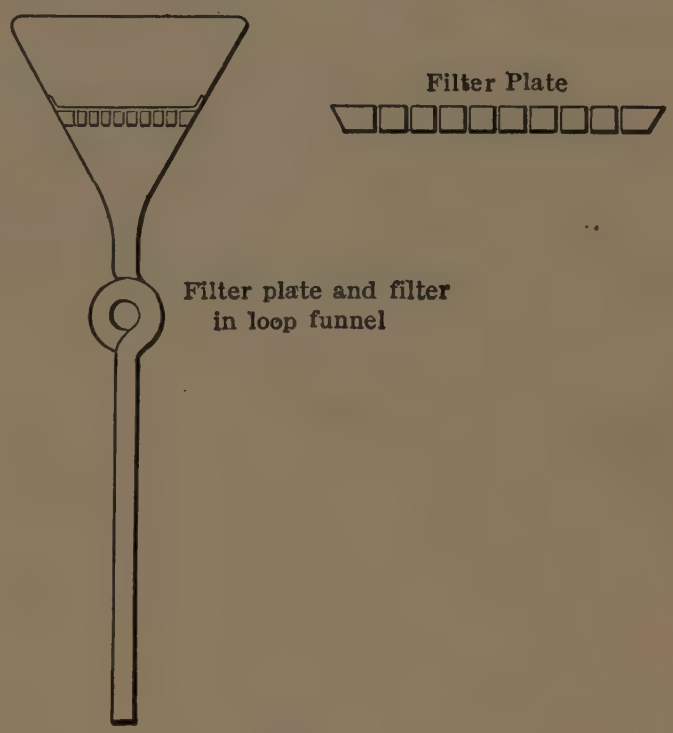


FIG. 4*a*.

To prepare the filtering arrangement, proceed as follows: Center the filter on the plate and wet it. Hold the funnel inverted and raise the plate and filter into place; still holding the arrangement secure, reverse the funnel to its proper position and then set it in its support. Prepare some paper pulp by violently shaking scraps of filter paper

in an 8-oz. stoppered flask with about 150 cc. of a mixture of 1 part strong hydrochloric acid and 2 parts water.* Pour a little of this pulp over the filter. Using an inverted wash-bottle, pour water into the funnel several times, allowing the filter to drain each time, to distribute the paper pulp and fill up any leakages around the edges of the filter.

Asbestos pulp may, of course, be substituted for paper pulp, if desired.

The above arrangement can be used to great advantage in many places where the directions in the text call for an ordinary filter.

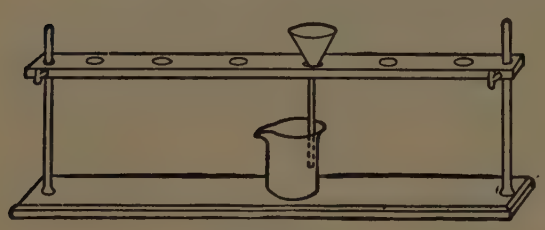


FIG. 5.

4. Funnel-support.—The support shown in the figure is very convenient. It holds six funnels in a compact row, which facilitates manipulation. (Fig. 5).

5. Cooling-box.—Considerable time can be saved in copper, lead and other determinations, where a hot liquid in a flask has to be cooled to ordinary temperature, by employing a cooling-box or tank of some sort. The one shown in Fig. 6 consists of a wooden box lined with sheet lead and provided with pipes for the entrance and overflow of cold water. The top board, covering half the opening, is secured in place and has openings for the entrance of 6 flasks. The inner end of each opening is enlarged somewhat and the board is cut away conically underneath, so that a flask which will float will rise into its socket and be in no danger of overturning.

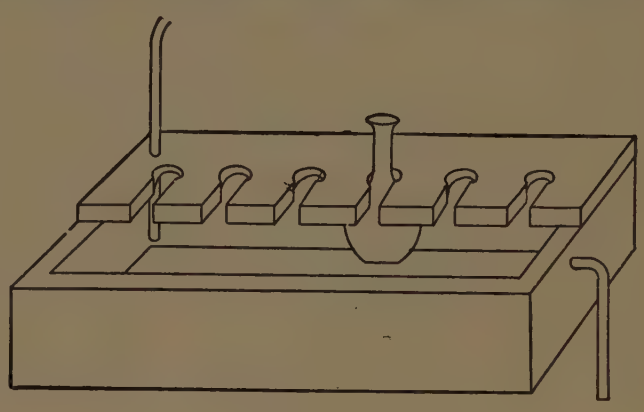


FIG. 6.

6. Hydrogen Sulphide Apparatus.—Notwithstanding all the automatic arrangements that have been devised for generating hydrogen sulphide, I prefer, for ordinary use in a small laboratory, the simple combination shown in Fig. 7. The generating bottle should be of convenient size, say 16-oz., and the stoppers rubber. The washing-

* This mixture tends to become slightly gelatinous on keeping. With hot water alone, more shaking is required, but the mixture will keep.

bottle is about half filled with water. It takes only a minute or so to clean and charge this apparatus, and when one has finished using it, the excess of gas can always be conducted into water to keep up the supply of hydrogen sulphide water. It is always advisable to clean the apparatus immediately after use, leaving it about half full of water containing a quantity of the iron sulphide. It is then ready for instant use at any time.

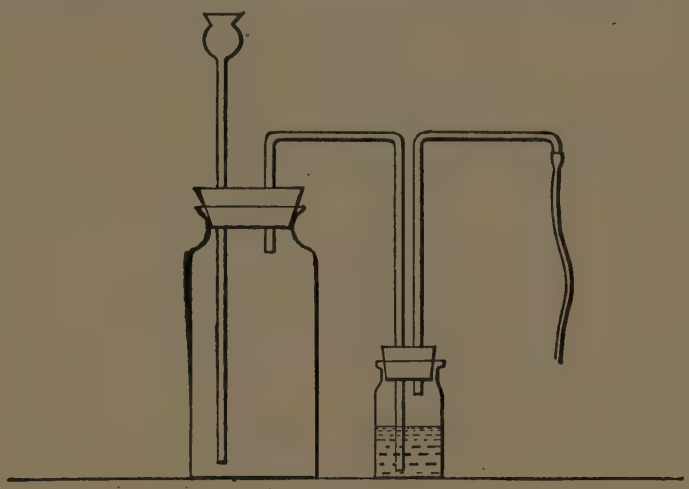


FIG. 7.

7. Measuring-glass.—For the best work it is indispensable that all reagents should be measured, so that no doubt may exist as to the amount used for any purpose. A 25-cc. measuring-glass is perhaps the most convenient size for constant use. It is an unfortunate fact that almost all measuring-glasses and casseroles seem to be made with the lip on the wrong side for the analytical chemist's use. In the case of the 25-cc. measuring-glass, it is a good plan to have a glass-blower flange the entire top, as shown in Fig. 8. This permits easy filling and pouring from all sides, and if the edge of the flange is made thin, liquids will not be very likely to run down the outside.

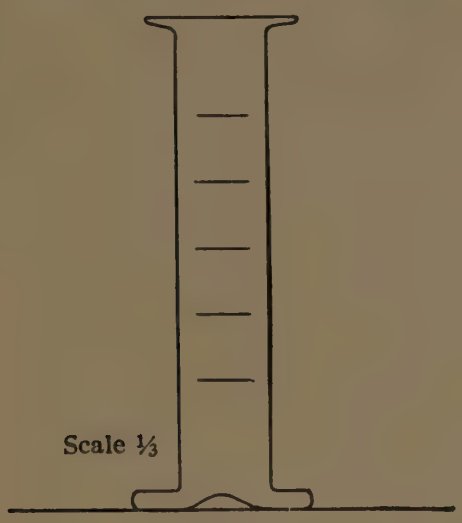


FIG. 8.

8. Flask-holder.—The holder shown in Fig. 9 is one of the most useful articles in my laboratory. My first holder came from Holland, and until the Denver Fire Clay Co. copied my model I was unable to obtain a duplicate in this country. It is the best design and the handiest to use of any I have seen. The portion that grasps the flask is lined with cork cemented in place with sealing-wax. A much cheaper and very satisfactory form of holder for students' use is shown in Fig. 9*a*. It is made from my design and kept in stock by the Denver Fire Clay Co.

9. Apparatus for Standard Solutions.—All kinds of arrangements have been devised for facilitating the filling of burettes from the

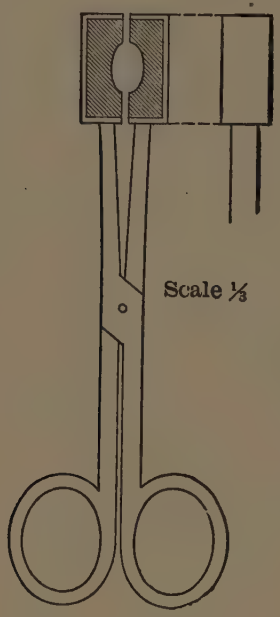


FIG. 9.

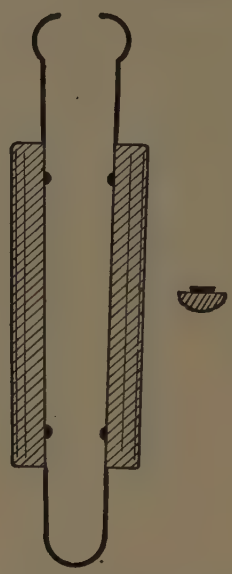


FIG. 9*a*.—Flask Holder.

stock bottles of standard solutions. Some of the methods are very convenient and satisfactory, but for the most accurate work with the least apparatus I prefer the following plan:

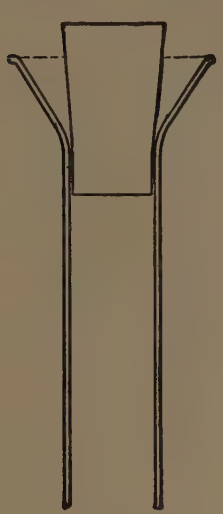


FIG. 10.

Keep the standard solutions in large stock bottles of about 9 liters capacity. From the large bottles fill smaller ones, say 1 liter size, as required. Have the burettes enlarged to a funnel shape at the top, as shown in Fig. 10, and keep them stoppered or covered with a cap when not in use. When a burette is to be filled the solution may easily be poured in from the small bottle. By this plan the liquid in a burette can always be mixed before use if desired, and the solution in the small bottle also shaken up. There are no stop-cocks or rubber tubes to keep in order and the solution in the large bottle is disturbed only when necessary to refill the small bottle.

10. Burette Pinch-cock.—For use with solutions that do not attack rubber, I know of no better pinch-cock than the one shown in Fig. 11. It consists simply of a rubber tube plugged with a short section of glass rod or a small bulb. By squeezing the tube around the plug between

the fingers slightly, a channel is made for the passage of the liquid. With a properly proportioned tube and plug the arrangement is very satisfactory.

11. **Surface of Work-table.**—The most satisfactory surface I have tried for the work-bench is asbestos-board, at least $\frac{1}{8}$ of an inch thick,—$\frac{1}{4}$ in. is better. It should be cut to fit the bench and laid in as large sheets as possible. It is usually unnecessary to tack it in place. Instead of covering the entire bench, it may suffice to cover a small section where the operator does most of his work. The outer edge that receives wear should be painted with melted paraffin. The entire surface may be rendered more durable by painting it with paraffin dissolved in carbon tetrachloride. The advantages of the asbestos surface are its comparative indestructibility under the action of corrosive chemicals or heated articles, its softness, which results in a saving of glass utensils, and, if it is not painted with paraffin, its rapid absorption of spilled liquids. When much soiled or worn it is easily renewed.

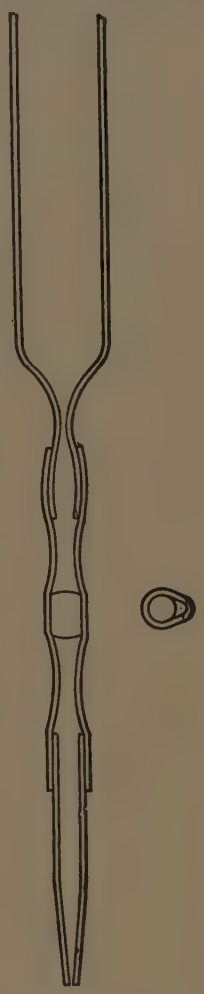


FIG. 11.

Linoleum likewise makes a very durable and satisfactory surface.

12. **Rapid Filtration of Gelatinous Precipitates.**—Dittrich * has described a method for the rapid filtration of gelatinous precipitates, such as ferric or aluminum hydroxide, which consists in mixing paper pulp with them before filtration. The paper pulp is prepared by violently shaking a piece of filter-paper with a little water in a small stoppered flask or bottle. The paper pulp does not ordinarily interfere with the subsequent ignition of the precipitate.

I have found the scheme very useful in certain cases. Where it is desired to keep the volume of the filtrate as small as possible, the mixed pulp and water may be first poured into the filter and the drained-off water thrown away. The filtration of the gelatinous mixture stirs up the pulp, which thus appears to be as effective as usual.

13. **Sand-bath.**—A "sand-bath," so-called, without the sand, supported on an iron tripod and heated with a Bunsen burner, is an

* Ber., 37, 1840.

excellent arrangement for flasks and casseroles. The bath is stamped from thin sheet-iron and is of circular form, about 5 in. in diameter and 1 in. deep. A piece of thin asbestos board placed in the bath under a flask, with a properly adjusted flame, will produce a mild diffused heat for gentle boiling to dryness, with the least liability to " bumping," or cracking the utensil after dryness is reached. For a silica evaporation the evaporating-dish may be supported on a scorifier placed in the sand-bath and a fairly strong flame used. This will effect a rapid evaporation without boiling, and the heat is sufficient for the subsequent dehydration of the silica.

FIG. 12.
Boiling Rod.

14. Boiling Rods.—For the prevention of " bumping " in boiling, glass rods with a short capillary tube on the lower end have been recommended. The objection to them is that it is difficult to wash out the capillary opening. To obviate this I have had rods made from glass tubing with a cup-shaped cavity in the end, as in Fig. 12, which permits of easy washing. The larger cavity appears to serve just as well as the capillary tube. Tubes, closed at both ends, are usually preferable to solid rods for ordinary stirrers.

15. Wash-bottle for Ammonia, etc.—To prevent the back-flow of corrosive vapors into the mouth I have found the arrrangement shown in Fig. 13 very satisfactory. The mouth-tube is of as large diameter as convenient, suitably contracted at the outer end, and extends to the bottom of the flask. The lower end is drawn out to a small opening and is slightly bent away from the exit tube, so as to prevent the blown-in air from entering the latter. It is not bent so much that it cannot be inserted through the stopper. The latter is pierced with a third hole which is covered by a piece of sheet-rubber. The sheet-rubber is cut to fit the top of the stopper and is held in place by the tubing. It serves as a valve for the third hole when manipulated by pressing and releasing with the finger. To use the bottle, close the valve and blow, taking care to release the valve before discontinuing

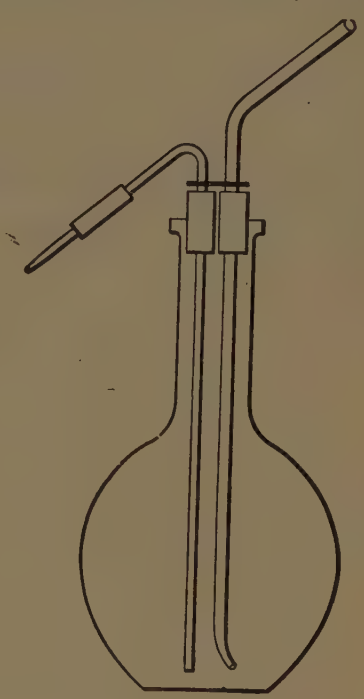


FIG. 13.

the pressure. The small opening in the lower end of the mouth-tube, together with the large diameter of this tube, will effectually prevent any residual pressure from forcing liquid back into the mouth. Do not have the small opening *too* small, so as to produce very slow action. The advantage of the above arrangement is its durability; it never gets out of order.

16. Pencil for Glass, etc.—For marking glass and porcelain, the blue pencils of a greasy composition, sold for the purpose, will be found most convenient. They are best sharpened with a coarse file.

17. Cleaning Solution.—Dissolve 5 grams of powdered commercial sodium dichromate in 500 cc. of commercial sulphuric acid. The solution may be used cold but is more effective when warm. It is poured through burettes and into flasks, etc., to remove organic matter and other films.

CHAPTER II

ELECTROLYSIS

THE following remarks on electrolysis are intended simply as an aid to those who have to make an occasional electrolytic determination. The apparatus necessary for making a single determination of copper, nickel, or bismuth is described, and a few general directions are given as to manipulation and the attainment of the proper conditions.

Those who desire to pursue the subject further or to fit up an elaborate installment are referred to the standard works on electrochemical analysis.

1. **Battery.**—Three $\frac{1}{2}$-gal. Grenet cells, French form. These will give all the electromotive force and current necessary. Both the electromotive force and the current can be sufficiently varied by using from 1 to 3 cells in series. The degree to which the zinc plates are immersed affects the current but slightly. The following solution is used in this battery: For each cell—water, 2 liters; strong sulphuric acid (commercial), 200 cc.; powdered potassium dichromate, 226 grams.

The zinc plates should be amalgamated with mercury. When the battery is not in use, it is best to remove and wash the carbons and zincs and cover the jars with watch-glasses.

2. **Volt-Ammeter.**—Some form of apparatus for measuring the current is quite necessary. Voltmeters and ampere-meters may be purchased as separate or combination instruments. A form of the latter, called the "Student's Volt-Ammeter," manufactured by the L. E. Knott Apparatus Co. of Boston, Mass., will serve very well for ordinary work. It costs about $7.

3. **Electrodes.**—One set of electrodes is sufficient for the determinations mentioned above, as follows: *Cathode.* A plain cylinder of platinum foil, 5 cm. long and 2.5 cm. in diameter. It has a total surface (including both sides) of about 78.5 sq. cm. and weighs about

12.5 grams. A stout platinum wire about 12 cm. long is attached to the top of the cylinder. *Anode.* This is made from a single piece of stout platinum wire. A straight portion about 17 cm. long rises from the center of a circular base, made by coiling the wire closely about itself, so as to form a disk about 2 cm. in diameter. It weighs about 8.5 grams.

FIG. 14.—Electrodes.

4. Beaker for Electrolysis.—This is about 5 cm. in diameter and 9 cm. high. A narrow strip of paper is pasted on the outside at the point indicating a volume of 100 cc. A 4-in. watch-glass split in two serves as a cover, the electrode wires passing through the crack in the center.

5. Supports for Electrodes and Beaker.—One of Classen's supports with two clamps (sold by dealers for about $4) will serve very well, or the operator can easily construct a support of wood and a few binding-posts. It is a good plan to have the beaker on a block of wood or other elevated support, so it can easily be raised into place or lowered away from the electrodes as desired. The elevated arrangement of the beaker will also permit of its being supported over a flame if a temperature higher than the ordinary is required.

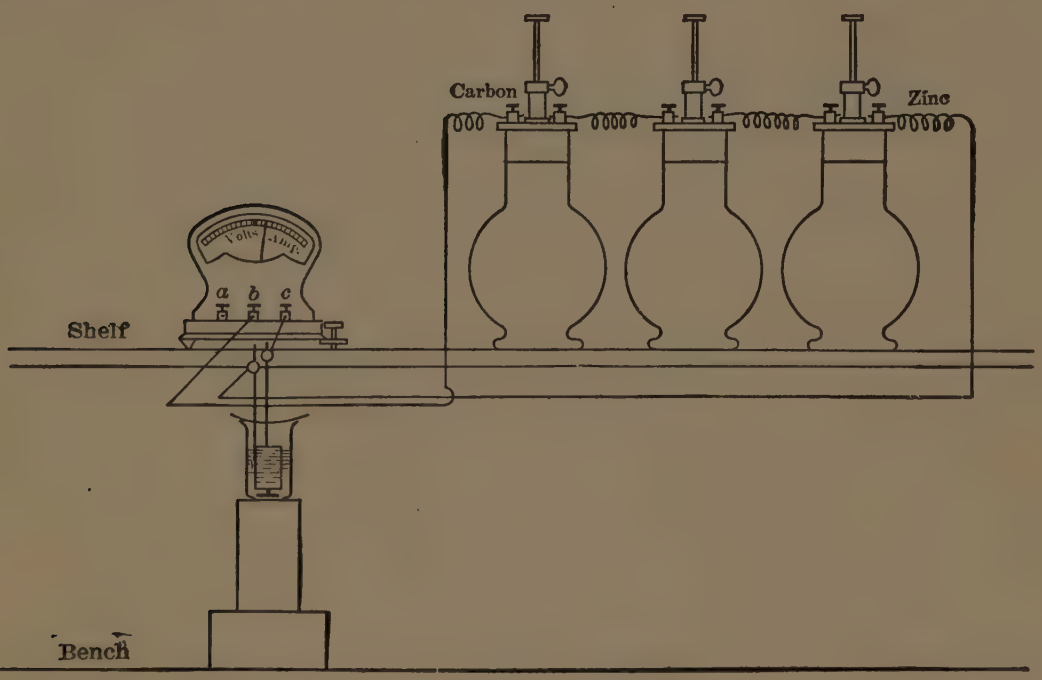


FIG. 15.

6. Figure 15 shows a convenient plan for a single apparatus. The battery and volt-ammeter are placed on a shelf over the work-

bench and the electrodes are held by two binding-posts screwed into the edge of the shelf, the connections being made as shown in the diagram. The figure is intended simply to show the arrangement, and in practice the wires may be more or less concealed and connected with convenient switches if desired. The beaker is supported on one or more wooden blocks resting on the bench, or a ring-stand may be used. When an electrolysis is finished, the beaker can be held in the hand while the block is removed, and then, with the current still passing, it may be gradually lowered from the electrodes, while the latter are washed with a stream from the wash-bottle. The beaker may then be replaced with one filled with distilled water before the cathode is disconnected. The volt-ammeter indicates amperes to the right and volts to the left of a central zero. The diagram shows the ammeter side in circuit, connections being made with the binding-posts *b* and *c* in series, and the needle inclined to the right. To read volts, connect the battery wires directly with the electrode binding-posts and attach shunt wires from these posts to *a* and *b*. When the proper connections are made the needle will point to the left.

7. Conducting an Electrolysis.—Clean and ignite the electrodes, and, when cool, weigh either one or both as required. Now, by means of the supports and binding-posts, adjust the electrodes and beaker of solution as follows: Place the anode within the cathode with its base perhaps a quarter of an inch below the lower edge of the cylinder. Adjust the beaker and volume of solution so that the anode nearly touches the bottom of the beaker, and the top of the cathode cylinder is about a quarter of an inch above the surface of the liquid. Cover the beaker with the split watch-glass and connect the electrodes with the battery. For copper, nickel, and bismuth the cathode is to be connected with the zinc pole.

Now include the ammeter in the circuit and note the reading. It is not sufficient to know simply the amount of current passing, since the actual effect of this current in the solution is governed by the area of electrode surface over which it is distributed. It is necessary to have a certain amount of current passing into a unit area of cathode surface in order to effect a proper deposition of metal; in other words, the current must have a certain *density*. One hundred square centimeters has been chosen as the unit area to which to refer the current as read in amperes. Thus, if a current of 2 amperes is received on 200 sq. cm. of cathode, the current density per 100 sq. cm.

is only 1 ampere. Conversely, if 1 ampere of current is passing through 50 sq. cm. of cathode surface the density per 100 sq. cm. is 2 amperes. The symbol ND_{100} is used to express the density of the current per 100 sq. cm. of electrode surface exposed to its action. When the area of the cathode (including both sides) actually immersed in the solution is known, the current density may be easily calculated from the reading of the ammeter. Thus, if the ammeter reads 2 amperes and the cathode has 75 sq. cm. of surface immersed, then $ND_{100} = \frac{2}{0.75}$, or 2.66 amperes.

If one cell fails to give a sufficient current, use two or three in series, as necessary. Under given conditions of resistance a certain electrode tension is required in order to obtain a stated strength of current. This tension may be measured with the voltmeter. The instrument is not, like the ammeter, included in the main circuit, but is placed in a shunt between the electrodes or points in the circuit whose difference of potential is to be measured.

Having attained the proper current conditions, it is best to leave the ammeter in the circuit during the entire electrolysis, so that any variation in the current may be noted and corrected if necessary.

When the appropriate tests show the metal to be all deposited, the beaker may be removed, and the electrodes washed as described above, or according to the directions given for the metal being determined.

It is usually best to wash the electrode to be weighed, first with distilled water and then with strong alcohol. It may then be drained a moment on filter-paper, dried by holding over a hot plate, or better, in a drying-oven at about 100° C., and finally cooled and weighed.

A cathode cylinder made of platinum wire gauze has been found to offer some advantages over one made of foil. A freer circulation of the solution is afforded, the time of deposition is shortened, and the deposited metal is more firmly adherent.

By the use of special apparatus arranged to rapidly rotate one of the electrodes, a very strong current may be employed without injuring the quality of the deposit, and the time required for a satisfactory electrolytic determination may thus be shortened to twenty minutes or less. Descriptions of such methods may be found in electrochemical literature.

CHAPTER III

LOGARITHMS

1. The ordinary calculations of technical analysis may be greatly facilitated by the use of logarithms; furthermore, the liability to error is considerably lessened on account of the fewer figures employed, and for the same reason a calculation is more easily checked over and any error detected.

When logarithms are not used it is a great advantage to have the standard solutions for volumetric work of certain exact strengths, so that their factors will be whole numbers. It is frequently difficult to prepare such solutions, and they are liable also to require troublesome adjustment from time to time. By the use of logarithms the necessity for these hard-and-fast standards is obviated, the calculation with any factor being very short.

Tables of logarithms and antilogarithms are given in this book, but for daily use it is best to have tables mounted on opposite sides of a piece of stout cardboard. They can be purchased in this form of the Franklin Laboratory Supply Co., 79 Amherst Street, Cambridge, Mass.

For the benefit of those who are unfamiliar with logarithms, or out of practice, the following remarks are appended:

To *multiply* two numbers, *add* their logarithms. The sum is the logarithm of the product.

To *divide* one number by another, *subtract* from its logarithm the logarithm of the divisor. The remainder is the logarithm of the quotient.

The logarithm of a number is composed of two parts—a positive or negative integral number called the *characteristic*, and a positive decimal fraction called the *mantissa*.

All numbers composed of the same figures placed in the same order have the same mantissa irrespective of the position of the decimal point.

The characteristic of a logarithm indicates the position of the decimal point in the corresponding number. When the number has one significant figure to the left of the decimal point, the characteristic of its log. is 0. If there are two figures it is 1, with three figures it is 2, etc. A decimal fraction has a negative characteristic which is equal to the number of places the first significant figure is removed from units; thus, the characteristic of the log. of 0.0459 is -2; of the log. of 0.0046, -3, etc. A negative characteristic is written with the minus sign immediately over it. It may be made positive by adding 10 to it, the fact being indicated by writing 10 with a minus sign after the mantissa.

The above rules may be illustrated as follows:

Number.	Logarithm.
4691	3.6713
469.1	2.6713
46.91	1.6713
4.691	0.6713
.4961	$\bar{1}$.6713 or 9.6713 − 10
.04691	$\bar{2}$.6713 or 8.6713 − 10
.004691	$\bar{3}$.6713 or 7.6713 − 10

The -10 after the mantissa is frequently omitted where the value of the characteristic is obvious.

In many simple operations the position of the decimal point may be seen at a glance without the use of characteristics. For instance, when working with a standard solution where 1 cc. = about 1 per cent of the constituent sought, then, if 45 cc. have been used and the figure corresponding to the log. obtained (no characteristics having been used) is 4563, it is evident that the percentage is 45.63 and not 4.56 or 0.45.

Four-place logarithm tables are intended to be used with numbers of not more than four figures. Such tables, however, will suffice for most of the calculations of ordinary analytical work.

To find in the table the mantissa of the log. of a number, proceed as follows: If the number consists of only one or two figures, find the number in the extreme left-hand column, and the mantissa will be given immediately opposite in the next column to the right headed 0. Thus the mantissa of the log. of 1 or 10 is .0000, of the log. of 12, .0792, etc. If the third and fourth figures of a number are 0, the mantissa

will also be in the 0 column as before. If the third figure is an integral number, the mantissa will be found in the same horizontal line, in the column headed with that figure; thus the mantissa of the log. of 124 or 1240 is .0934. If the fourth figure of a number is an integral number, recourse must be had to the column headed "Proportional Parts." When the mantissa for the first three figures has been found, there must be added to it the amount found in the same horizontal line in the column headed with the fourth figure in the proportional parts. Thus the mantissa of the log. of 1245 is .0934+.0017, or .0951. Having found a required mantissa, prefix the characteristic according to the rules given above.

The table of antilogarithms gives the numbers corresponding to logarithms, and a number is found from its logarithm in precisely the same manner as a logarithm is found in the table of logarithms. Thus the number corresponding to log. 9.0974 is 0.1251, the characteristic 9 signifying the same as $\bar{1}$ and indicating the position of the decimal point. In the same way log. 1.0974 gives 12.51, etc.

CHAPTER IV

ALUMINUM

1. The technical determination of aluminum (usually required as Al_2O_3) in ores and metallurgical products is a somewhat troublesome proposition. There seems to be no short and satisfactory method that is applicable to complex substances. The usual interfering elements are iron, manganese, arsenic, antimony and phosphorus. Chromium and titanium would prove sources of trouble, but are so rarely present in ordinary ores that they may usually be neglected. There are two general methods of procedure, the direct and the indirect. In the direct method the aluminum is weighed as $AlPO_4$ or Al_2O_3. In the indirect method the aluminum, iron, and perhaps phosphorus are weighed together as Al_2O_3, Fe_2O_3 and P_2O_5, the latter, of course, combined to form a phosphate with the others. The alumina is then found by difference, after the weight of the other constituents of the mixture has been determined and deducted.

2. **Direct Method.**—Treat 0.5 gram of the ore in a platinum dish with 2–3 cc. of strong sulphuric acid and about 20 cc. of strong pure hydrofluoric acid.[1] Evaporate over a water-bath or other gentle heat as far as possible, and then cautiously raise the heat until the sulphuric acid is fuming copiously. Allow to cool, add water and a little hydrochloric acid and warm the mixture until the dish is free from adhering insoluble matter. Now transfer, using as little wash-water as possible, to an 8-oz. flask. Add 5 grams of potassium sulphate, 5 cc. of strong sulphuric acid and one-eighth of a 9-cm. filter. Boil the mixture gently at first, to expel water and hydrochloric acid, then, as the sulphuric acid begins to fume, the heat may be increased as strongly as the prevention of undue foaming will permit, finally with the flask in a holder, over a free Bunsen flame, until any free sulphur is entirely expelled and the separated carbon is completely oxidized, leaving a clean mass or melt, with but little free sulphuric acid. Allow the flask to cool in an inclined position to avoid cracking. The object of the filter paper is to reduce any arsenic or antimony to

the *ous* condition, and thus render its subsequent precipitation as sulphide rapid and complete.[2]

3. After cooling, add 150 cc. of water and 5 cc. of strong hydrochloric acid and warm the mixture until everything soluble has dissolved. If a trifling residue remains it may usually be neglected. From a larger residue, decant most of the solution through a filter and heat the residue with dilute hydrochloric acid, repeating these operations once or twice if necessary. Calcium sulphate or lead salts may thus be dissolved or greatly reduced in amount.[3] Pour the solutions through the filter, finally transferring any remaining residue, and wash with hot water. Reserve the filtrate. The final residue may consist of a little barium or calcium sulphate or other unimportant substance. If its character is thus recognized it may be neglected, but if this is uncertain and aluminum is likely to be present, it is best to treat it further. Ignite filter and contents in a platinum dish until the carbon is consumed. The residue may now be either again evaporated with a little hydrofluoric and sulphuric acid nearly to dryness, or, if silica is apparently absent, it may be fused with a little mixed sodium and potassium carbonates.[4] In either case the solution of the product, acidified with hydrochloric acid, may be added directly to the reserved filtrate, without regarding any residue of barium sulphate.

4. The liquid is now an acid solution of the various bases. It should not be too acid, and it is therefore safer to nearly neutralize with ammonia and then reacidify with an excess of 5 cc. of hydrochloric acid.[5] Now dilute to about 300 cc. with hot water and pass in hydrogen sulphide to precipitate the metals of that group. Ten minutes will usually suffice for this precipitation, since any arsenic or antimony is in the *ous* condition and will come down quickly. It is well, however, to have the liquid fairly cool at the end, to ensure the complete precipitation of any lead. Filter, washing with water containing hydrogen sulphide and a little acetic acid. Boil the filtrate until all hydrogen sulphide is expelled and then oxidize the iron to the ferric condition by the cautious addition of 10 cc. of bromine water to the boiling solution.[6] Now dilute to about 400 cc. with cold water and allow to cool to room temperature. The liquid is now ready for the precipitation of the aluminum as phosphate, according to Peters's modification of Wöhler's method,* as follows:

* Blair, Chem. Anal. of Iron, 3d ed., p. 250.

5. Add ammonia until the solution becomes brown or dark red in color, according to the amount of iron present, but still contains no precipitate. When there is little or no iron, simply neutralize to faint acidity, using litmus paper. Now add 3.3 cc. of hydrochloric acid of 1.2 sp. gr. and 2 grams of sodium phosphate dissolved in water and filtered if necessary.[7] Stir until any precipitate formed is dissolved and the solution becomes perfectly clear again.* Now add 10 grams of sodium thiosulphate, dissolved in water (and filtered if necessary), and 5 cc. of 80 per cent acetic acid, or 4 cc. of the 99 per cent acid. Heat to boiling, boil fifteen minutes,† and filter as rapidly as possible on an ashless filter.[8] Wash thoroughly with hot water. If the amount of the precipitate is small it may at once be dried, ignited in a porcelain crucible, together with the filter, and weighed as $AlPO_4$. Multiply this weight by 0.4183 to obtain the weight of the Al_2O_3.[9]

If the precipitate is large in amount it should be redissolved and reprecipitated. Rinse it into a beaker, add a little hydrochloric acid to dissolve it, and then pour through the filter, to dissolve what was not rinsed off, and wash the filter thoroughly. Dilute the filtrate somewhat, if necessary, add ammonia in slight excess, and then reacidify with acetic acid in slight excess. Heat to boiling, filter, and wash with hot water. Then dry (I have found this apparently unnecessary), ignite, and weigh as above described. It is always well to again boil the filtrate from the first precipitate of aluminum phosphate for some time and filter off the precipitate formed on a separate filter. Ignite this in a separate crucible (not weighed), and if any $AlPO_4$ is found, brush it in with the main portion. A precipitate of sulphur will thus always be obtained, and the presence of aluminum phosphate can be determined only by igniting it. It is best to repeat this boiling and filtering until the ignited precipitate leaves no residue.

---

[1] Alumina compounds in ores are very likely to consist of silicates not easily decomposed by ordinary acids. The hydrofluoric acid used decomposes these silicates and the sulphuric acid eventually expels the hydrofluoric acid and converts the bases to sulphates. The material is now in condition for the treatment

* Blair's directions. Personally, I have frequently found the solution to become more and more turbid. I then cautiously add more hydrochloric acid until the solution clears, note the extra amount used and increase the sodium thiosulphate at the rate of 10 grams for each 3 cc. of acid required.

† Blair's directions. I have found thirty minutes safer.

in a flask that follows. This treatment is given to complete the decomposition and facilitate subsequent operations.

[2] If arsenic is left in the *ic* condition, its precipitation by hydrogen sulphide is very slow, as the hydrogen sulphide has to first reduce it to the *ous* condition.

[3] The heating with sulphuric acid and potassium sulphate converts any iron present into anhydrous ferric sulphate. This is usually the most troublesome of the eventually soluble salts to get into solution, as it first has to become hydrated. Even by heating in the presence of hydrochloric acid the solution is frequently very slow. Undissolved anhydrous ferric sulphate, when much is present, usually appears as minute pearly scales by slowly rotating the liquid. When allowed to settle it is not as white as the sulphates of barium, calcium or lead. Any remaining undissolved is liable to retain aluminum sulphate and thus render the result low.

[4] The mixed salts are used simply because they fuse at a lower temperature than the single salts.

[5] If the solution is very acid, hydrogen sulphide may fail to completely precipitate all the metals of the group.

[6] Hydrogen sulphide reduces any iron present to the ferrous condition. Bromine water is added to oxidize the iron back to the ferric state. If the hydrogen sulphide were not previously boiled off it would be decomposed by the bromine water and produce an unnecessary precipitation of sulphur. Having the iron in the ferric state permits the proper neutralization with ammonia without causing any of the iron to precipitate. When the cold ferric solution is gradually neutralized with ammonia a soluble brown basic ferric chloride is eventually formed, the neutralization being carried to the extreme that will not cause a precipitation.

[7] The hydrochloric acid added prevents the precipitation of ferric phosphate by the sodium phosphate. When the thiosulphate is added, it completes the neutralization of the mineral acids and sets free sulphurous acid in their place, at the same time reducing the iron to the ferrous condition. Ferrous phosphate is soluble under these conditions and therefore does not precipitate. Acetic acid is added to maintain the presence of a weak acid during the subsequent boiling and thus prevent the precipitation of all other phosphates except aluminum phosphate.

[8] Aluminum phosphate is more or less soluble in cold dilute acetic acid and therefore does not precipitate at once. In the same mixture, heated to boiling, however, it is quite insoluble and comes down together with sulphur that separates from the continually decomposing thiosulphate. Sulphur always precipitates even in the absence of aluminum. It is white at first and therefore indistinguishable from the white aluminum phosphate, but agglomerates and turns yellowish on prolonged boiling. Its admixture with the aluminum phosphate is advantageous, as it facilitates filtration and washing. The filtration is made without delay, while the liquid is boiling hot, on account of the possibility of some of the aluminum phosphate dissolving if the solution is allowed to cool. Even when the precipitation of the aluminum has been complete, the filtrate always becomes turbid owing to the continued precipitation of sulphur.

[9] The sulphur all burns off during the ignition, and the formula of the ignited

residue is $AlPO_4$. Its molecular weight is 122.14. Two molecules of $AlPO_4$ correspond to 1 molecule of Al_2O_3, of which the molecular weight is 102.2. This gives the proportion 244.28 : 102.2 = 1 : x. x = 0.4183. That is, any weight of $AlPO_4$, multiplied by 0.4183, will give the weight of Al_2O_3 to which it corresponds.

For the treatment in the flask, potassium sulphate is prescribed. Potassium or sodium acid sulphate, or anhydrous sodium sulphate will serve equally well. Acid sulphates are unnecessary at the outset, as normal sulphates are soon converted to acid sulphates by the concentrated sulphuric acid and heat.

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6. Direct Method Using Sodium Thiosulphate.—Proceed as described in **2**, **3** and **4** until the liquid of **5** is obtained. Now add dilute ammonia cautiously, with stirring, until the precipitate produced finally dissolves with difficulty, but avoid causing a permanent precipitate. Endeavor to have the solution now contain not over 100 mg. of Al in 200 cc. Add an excess of sodium thiosulphate and boil until free from SO_2. $Al(OH)_3$ is precipitated together with free sulphur, according to the reaction:

$$2AlCl_3 + 3Na_2S_2O_3 + 3H_2O = 2Al(OH)_3 + 3SO_2 + 3S.$$

Filter the precipitate of $Al(OH)_3$ and sulphur and wash thoroughly with hot water containing some ammonium chloride or nitrate. Dry the precipitate, separate it from the filter, ignite the latter and add the ash to the main precipitate. Now ignite the whole over the blast lamp to constant weight and weigh as Al_2O_3. The above procedure separates aluminum from iron.

7. Indirect Method.[1]—This is useful in technical work only when the precipitate of mixed iron and aluminum hydroxides can be easily obtained free, or nearly so, from phosphorus and arsenic, as in the case of clay and similar material. If phosphorus or arsenic are likely to be present in more than negligible amount, their separation or estimation is involved, and the process usually becomes too tedious for a technical method. Where the method is applicable the procedure may be as follows:

Take 0.5 gram of the substance and decompose it, according to its nature, either with acids or by fusion in platinum with a mixture of 3 grams of sodium carbonate and 2 grams of potassium carbonate.[2] In the latter case, fuse until clear, disintegrate the cold melt by heating with water and transfer the mixture to an evaporating-dish. Cover the dish, acidify with hydrochloric acid and evaporate to dryness to

remove silica. If acids alone have sufficed for the decomposition, the solution may be similarly evaporated. Sometimes an evaporation to dryness, in platinum, with hydrofluoric acid mixed with hydrochloric or a little sulphuric acid (the material being moistened with the latter before the hydrofluoric acid is added)[3] may serve to decompose the substance and remove silica at the same time. After the evaporation take up in hydrochloric acid and dilute. Dilute the filtrate from the silica, or the solution otherwise obtained free from silica, to from 100 to 300 cc., according to the amount of iron or aluminum apparently present, make slightly alkaline with ammonia and heat to boiling. Keep at a boiling temperature for a short time, then remove from the heat and allow to settle somewhat, and filter, washing with hot water. If the amount of the precipitate is large it is best to redissolve it in hydrochloric acid and repeat the precipitation. It is always safer to do this in any case.[4] The final washing should be very thorough, ten to twenty times with hot water, or until a portion of the filtrate shows no test for chlorine. Finally, dry and ignite the mixed hydroxides and weigh as Fe_2O_3 and Al_2O_3.[5] After weighing, fuse in platinum with a little potassium acid sulphate, take up the melt in dilute hydrochloric acid and determine the amount of Fe_2O_3 volumetrically, thus arriving at the weight of the Al_2O_3 by difference.[6] Phosphours, arsenic, and the heavy metals are presumably absent from the substance tested. If manganese is present in appreciable amount it should be separated from the iron and aluminum by the basic acetate method (see Fresenius or Treadwell) previous to the precipitation by ammonia.

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[1] Frequently, in analytical separations, the precipitate which is produced by ammonia, or bromine (to catch manganese) and ammonia, and which consists mainly of the hydroxides of iron, aluminum and manganese, is so slight that it is simply ignited and weighed without an attempt at separation. It is then reported either as Fe_2O_3 or Fe_2O_3, Al_2O_3, and perhaps Mn_3O_4 also.

[2] The mixed carbonates fuse at a lower temperature than either salt separately. With silicates very difficult to decompose, it is better to use sodium carbonate alone and a higher temperature.

[3] If hydrofluoric acid is added before moistening with sulphuric acid, the heat of combination with the silica of the powdered material is liable to produce a puff of vapor sufficient to cause a loss of some of the substance.

[4] Iron and aluminum, when precipitated in the ordinary way with ammonia, usually carry down with them some of the other constituents in solution, such as

calcium, copper and zinc. Even though the salts thus carried down are soluble, they cannot subsequently be washed out of the precipitate. When the precipitate is large and the impurities are non-volatile, a considerable error may be introduced. Re-solution of the precipitate, followed by a second precipitation, minimizes this error. Sometimes a third or fourth treatment is desirable. Alumina, after ignition, is very hygroscopic, and therefore no time should be lost, after cooling in a desiccator, before weighing. The ignited precipitate is liable to gain weight after cooling, even when in a desiccator.

[5] Suppose that the weight of the combined oxides was 0.1062 gram. On the 0.5 gram basis this is equal to 21.24 per cent. Inspection will sometimes show whether Fe_2O_3 or Al_2O_3 preponderates, the former being brown and the latter white. If the amount of iron present is apparently very small, its determination is best made by varying the usual precedure somewhat. Consult IRON, **13**, at end, and **14**. The above residue has been gotten into hydrochloric acid solution. Add a small pinch of granulated zinc. The mixture soon becomes colorless, showing that the iron is all reduced. Add a little sulphuric acid to dissolve the excess zinc, then dilute with cold water to perhaps 50 cc. and filter, receiving the filtrate in a beaker. See that the solution is cold, and titrate at once with standard permanganate. Special refinements as to bulk of solution, degree of acidity and blank test of the zinc are unnecessary.

When the amount of iron is apparently large, treat the hydrochloric acid solution just as described in IRON, **13**, at end, and **14.**

[6] Suppose, on the basis of 0.5 gram of ore taken originally, the titration showed 13.86 per cent Fe. This must be calculated to the corresponding per cent of Fe_2O_3, to make the proper subtraction from the per cent of the mixed oxides. The atomic weight of Fe is 55.84. The molecular weight of Fe_2O_3 is 159.68. It takes 2Fe to correspond to Fe_2O_3; therefore, $111.68 : 159.68 = 13.86 : x$. $x = 19.84$. This is the percentage of Fe_2O_3 in the mixed oxides. Total percentage, 21.24, minus $19.84 = 1.40$, the percentage of Al_2O_3.

CHAPTER V

ANTIMONY

THE technical determination of antimony in ores, etc., is best made by volumetric methods. The most troublesome interfering element is usually arsenic. Where arsenic is known to be absent or negligible, the procedure in the following method may be shortened by omitting the operations for its removal.

1. Before beginning treatment the nature of the material should be considered. Most sulphides and mixed ores yield readily to the acid treatment described below, but oxidized ores rich in antimony may fail of complete decomposition. Such material is easily decomposed by the method described in **6**.

2. **Method Applicable to Sulphides and Most Mixed Ores and Low-grade Oxides.***—Weigh 0.5 gram of the finely ground ore into an 8-oz. flask (a Pyrex flask is best), add 2 grams of anhydrous sodium sulphate, 5–6 cc. of strong sulphuric acid and one-eighth of a 9-cm. filter paper. The object of the latter is to provide organic matter for the reduction of arsenic and antimony to the *ous* condition, thus facilitating the solution of the antimony and also rendering the subsequent precipitation of both metals as sulphides rapid and complete. Heat the mixture, cautiously at first, over a small free flame, then, with the flask in a holder, over the full flame of a Bunsen burner. Continue until any free sulphur is all expelled, the separated carbon completely oxidized and the free sulphuric acid almost entirely driven off. If apparently necessary, add a little more sulphuric acid and run down again.

Allow the mass to cool with the flask on its side, as otherwise the solidifying cake may crack it, or, rotate the flask slowly with the holder until the mass solidifies on the sides.

3. When cold, add 25 cc. of hot water and warm gently, without boiling, to completely disintegrate the cake. Boiling would materially alter the volume of the water and change its relation to the hydrochloric acid next added. Remove from the heat, add 50 cc. of strong hydrochloric acid and agitate gently, without further heating, to dis-

* A. H. Low, Jour. Am. Chem. Soc., XXVIII, 1715, modified.

solve soluble salts, especially anhydrous ferric sulphate.[1] The mixture is now 2 volumes of strong acid to 1 of water.[2] Additional heating is avoided at this stage, as it might easily occasion loss of arsenic by volatilization, if the latter is to be determined, and might also change the relative proportions of acid and water, upon which the separation of arsenic depends.

Pass in a rapid current of hydrogen sulphide for about ten minutes. As any arsenic present is in the *ous* condition, this should be sufficient time for its complete precipitation. A little arsenious chloride in the vapors might permit the formation of sulphide that would escape from the flask. To prevent this possible slight loss it is best to use the arrangement shown in Fig. 16. The thistle-tube contains a few bits of broken glass moistened with 5 per cent sodium hydroxide solution. Any arsenic escaping is thus caught and subsequently recovered. Some copper may be precipitated, but no antimony or tin. During the precipitation make a mixture of 25 cc. of water and 50 cc. of strong hydrochloric acid, to be used in the subsequent washing. Also prepare a Witt's plate filter in a loop funnel (APPARATUS, 3). If a bell-jar and glass plate are available, so as to permit filtration into a beaker, they may be used with suction, but a filter flask is undesirable, as it necessitates subsequent transference of the filtrate into a beaker. The suction of a loop funnel is usually quite sufficient.

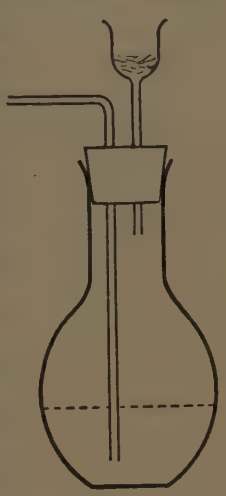

FIG. 16.

Filter off the As_2S_3 precipitate, receiving the filtrate in a 600-cc. beaker. Adhering sulphide in the flask or on the delivery tube will be recovered later, but it must be well washed with the acid mixture, to remove antimony.

Wash the delivery tube, held over the flask, with the prepared acid mixture and set it aside temporarily. Now wash out the flask with the same mixture, pouring from the flask over the precipitate, and allowing the filter to drain completely between washings. The antimony is now in the filtrate. If arsenic is to be determined, proceed with the precipitate, flask and delivery tube as directed in ARSENIC, 2.

Continue with the antimony as follows:

4. Mark the height of the filtrate on the beaker and then dilute with hot water to about $3\frac{1}{2}$ times this height. Pass in a rapid current of hydrogen sulphide for at least ten minutes. The previous delivery

tube and flask, if not reserved for arsenic, may be cleansed with ammonia and used for antimony. Filter the precipitated Sb_2S_3 through a Witt's plate filter as before, into a large beaker. The filtrate should be perfectly clear—otherwise re-filter. Using hydrogen sulphide water slightly acidified with acetic acid, wash out the beaker and delivery tube and then wash the precipitate six or seven times. This is to remove most of the hydrochloric acid. Reject the filtrate. Wipe out any adhering sulphide in the beaker with a bit of filter paper and place on the precipitate. Reserve the delivery tube.

Place the clean original flask, or a similar one, under the funnel. Warm about 15 cc. of a 5 per cent solution of sodium hydroxide in a small beaker. Cleanse the delivery tube, held over the funnel, with a few drops of this, and then continue to pour the solution very slowly over the precipitate to dissolve it. Use as little as possible—perhaps 10 cc. Dilute the remainder (or take a little more if necessary) with about 50 cc. of hot water, for washing. Wash the filter six or seven times with this, keeping the bulk of the filtrate as small as possible.

Add to the solution in the flask about 2 grams of anhydrous sodium sulphate and 6–7 cc. of strong sulphuric acid. Support the flask over a small free flame and boil down to small bulk; then, with the flask in a holder, run down, over a strong free flame, as in the original decomposition of the ore, using the same precautions in the cooling. The piece of filter paper for reduction purposes is here omitted as unnecessary.[3]

To the cool residue in the flask add 50 cc. of hot water and 10 cc. of hydrochloric acid, also about 3 grams of powdered tartaric acid, to prevent the separation of any insoluble antimonyl chloride. Heat to effect solution and then boil a short time to expel any possible SO_2. Now add 10 cc. more hydrochloric acid and cool completely under the tap. Dilute to about 140 cc. with cold water, and titrate with standard potassium permanganate solution to the usual pink tinge.[4] The end-point is sharp, but soon fades, owing to the action of the hydrochloric acid present.

The standard permanganate used for the iron titration will serve for antimony. The Fe value of the permanganate multiplied by 1.076 will give the Sb value.[5] Or, multiply the sodium oxalate ($C_2O_4Na_2$) value by 0.8971.

5. **Notes.**—Sometimes an appreciable amount of undecomposed material remains after the above fusion in a flask. This is usually of a silicious nature and not likely to contain antimony (or arsenic).

A small amount of copper (frequently present) has no influence on the antimony titration.

Tin is without influence on the antimony result (since it exists in the final solution as stannic sulphate), but it may prove a great annoyance, if much is present, owing to its troublesome sulphide. In such a case I have found Clark's oxalic acid method for preventing the precipitation of tin sulphide very satisfactory. Simply dissolve 10 grams of oxalic acid crystals in the filtrate containing the antimony, previous to diluting and passing in hydrogen sulphide. The tin will be kept in solution and occasion no further trouble.

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[1] In a hydrochloric acid mixture of this strength, antimony will not be precipitated by hydrogen sulphide, while arsenic in the *ous* condition will quickly come down as As_2S_3.

[2] Anhydrous ferric sulphate, produced by the effect of concentrated sulphuric acid and heat on iron salts, is most troublesome to dissolve. If much is present it appears as minute pearly scales when the liquid is slightly agitated or rotated. In a warm acid solution it will gradually become hydrated and dissolve.

[3] The free sulphur which is always present is a sufficient reducing agent, and, moreover, the antimony is already in a reduced condition at the outset.

[4] Antimony may be assumed to exist in the *ous* condition as $SbCl_3$, which the permanganate oxidizes to the *ic* condition, $SbCl_5$. The following explanation will serve to show how this is done. The reactions given are simplified so as to indicate only the essential points.

First, considering the permanganate:

$2KMnO_4 = K_2Mn_2O_8 = K_2O.Mn_2O_7$. The essential portion of this compound is the Mn_2O_7. This gives up oxygen and becomes reduced to Mn_2O_2, or, $2MnO$. $Mn_2O_7 = 2MnO + O_5$. This means that $2KMnO_4$ has 5 oxygen atoms available for oxidation. Now consider how one of these atoms can act on the hydrochloric acid present. $2HCl + O = H_2O + Cl_2$. This gives the chlorine necessary to change $SbCl_3$ to $SbCl_5$.

Of course, the antimony is oxidized without actually combining with any oxygen, simply by having its valence changed.

[5] It will be observed in the above reactions that 1 atom of oxygen serves to change $SbCl_3$ to $SbCl_5$, that is, O corresponds to Sb. For convenience we may say O = Sb. Now, when ferrous iron is oxidized by permanganate, or anything else, to ferric iron, no matter what the actual iron salts happen to be, the oxygen required is precisely the same in amount as though FeO were changed to Fe_2O_3. This reaction is $2FeO$, or, $Fe_2O_2 + O = Fe_2O_3$. This shows that every Fe_2 requires 1 oxygen, or $O = 2Fe$. Thus we have O = Sb and O = 2Fe, or, Sb = 2Fe. Considering the atomic weights, 120.2 parts of Sb = 111.68 parts of Fe by weight. Accordingly, if 1 cc. of an oxidizing solution like permanganate has a certain value for iron, its value for antimony will be in accordance with the proportion 111.68 : 120.2 = 1 : x. $x = 1.076$. The proportion for oxalic acid or an oxalate may be similarly calculated from the oxygen ratios.

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6. Decomposition of Oxidized Material.—In a thin spun-iron crucible of about 60-cc. capacity melt about 8 grams of sodium hydroxide (2–3 in. of the stick hydroxide, broken into short pieces). Heat until the moisture is expelled and quiet fusion attained, and then allow to cool. It is a good plan to add a very small pinch of potassium nitrate to the melt just previous to cooling, to guard against any subsequent reduction of metal from the ore.[1]

Weigh 0.5 gram of the powdered ore, transfer it to the prepared crucible, cover with a very loosely fitting porcelain cover and fuse the mixture. Heat very cautiously at first until violent bubbling has ceased, and then with the full flame of a Bunsen burner until quiet fusion is attained. Remove the cover and pour the melt upon a clean iron plate, or other cold smooth surface. Invert an evaporating dish over the hot cake, to prevent loss in case the cake cracks violently apart on cooling.

Set the crucible in a 400-cc. beaker containing 50 cc. of cold water. Cover the beaker and tip the crucible over with a glass rod, so as to admit the water, and add 40 cc. of strong hydrochloric acid. Warm the mixture and turn the crucible about with the glass rod until it appears clean. Remove and rinse the beaker cover, lift the crucible on the rod, and wash off the outside so as to permit handling with the fingers. Now rinse out the inside of the crucible. If any undissolved melt remains, dissolve it with a little hydrochloric acid and rinse into the beaker. Add the cooled melt and porcelain cover, and again cover the beaker. Warm until the cake has dissolved. Lift out the crucible cover with forceps, or by means of a bent iron wire passed through the loop, and wash it.

As a rule the decomposition is perfect and everything goes into solution in the hydrochloric acid, even the silicic acid, except, perhaps, scales of iron oxide from the crucible, to which no attention need be paid. Barium might separate as sulphate, but this is easily distinguishable from undecomposed ore. Now add 2–3 grams of tartaric acid,[2] and when it has dissolved, dilute sufficiently and filter if necessary, which is rarely the case. If gelatinous silica clogs the filter, a few drops of hydrofluoric acid will usually clear it.

7. Treatment of Solution.—Having obtained a hydrochloric acid solution containing all the antimony, together with sufficient tartaric acid, dilute to about 300 cc. with hot water. Precipitate the antimony with hydrogen sulphide and then follow the directions given in 4 up to the point where the cold residue is obtained in the flask after the

sulphate fusion. From this point, proceed exactly as after the fusion of the ore by the previous method.

8. Method for Hard Lead, etc.—In the absence of arsenic, treat 0.5 gram of the alloy, which may be in moderately coarse particles, precisely as described for ores in **2**, until the usual melt is obtained. When cold, add 50 cc. of hot water, 10 cc. of hydrochloric acid and about 3 grams of tartaric acid. Heat to effect solution and boil to expel any possible SO_2. Now add 10 cc. more hydrochloric acid and cool completely, under the tap. Dilute to about 140 cc. with cold water, and titrate with standard potassium permanganate solution to the usual pink tinge. Calculate the result, as in **4**. Tin, lead and small amounts of copper and iron do not interfere.

If arsenic is likely to be present, separate it just as described for ores in **2**. An alloy containing a large amount of copper should be similarly treated.

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[1] The sodium hydroxide contains an excess of water, which it does not give up until melted and heated to dull redness. Unless this water were removed before adding the ore, there would be a large loss from spattering. Sodium peroxide does not have this defect, but, on the other hand, its high oxidizing power in many cases prevents or hinders complete decomposition of the ore.

[2] This is to prevent the precipitation of a basic salt of antimony when the solution is subsequently largely diluted.

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9. Another Method for Hard Lead, etc.—Treat 0.5 gram of the very finely divided alloy in an 8-oz. flask with a mixture of 5 cc. strong nitric acid, 10 cc. of water, and 2–3 grams of tartaric acid.[1] Heat gently until solution is complete and then boil off most of the nitric acid. Add sufficient water (and more tartaric acid if the solution becomes turbid) and pour the mixture slowly into a solution containing 20–25 grams of sodium monosulphide and 10 grams of sodium hydroxide in 300 cc. of water.[2] Warm the mixture, allow the lead sulphide, etc., to settle, and filter, washing with water containing sodium sulphide. Make the filtrate slightly acid with dilute sulphuric acid, allow the precipitated antimony sulphide to settle, and then filter and wash with dilute hydrogen sulphide water. Treat the antimony sulphide from this point as described in **4**, or, if arsenic is likely to be present, proceed as follows: Rinse the precipitate from the filter as completely as possible, with a jet of hot water, into a 400-cc. beaker. Place the beaker and contents under the funnel and dissolve the precipitate still adhering to the filter with a little warm ammonium sulphide solution. Make the mixture in the beaker just

acid with hydrochloric acid and then add to it just double its volume of strong hydrochloric acid.[3] Warm the mixture slightly and stir until all the antimony sulphide has dissolved and then pass in hydrogen sulphide to again precipitate any arsenic sulphide that may also have dissolved. Finally continue as described in **3** and **4.**

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[1] The tartaric acid is added to prevent the precipitation of a basic salt of antimony.

[2] Sodium monosulphide holds the antimony in solution, while the sulphides of lead, copper, etc., precipitate. The monosulphide is preferable to a polysulphide for this purpose, mainly because, when the filtrate is subsequently acidified, there is less separation of free sulphur.

[3] In dilute acid solution both antimony and arsenic are precipitated by hydrogen sulphide, but in a mixture of the strength here prescribed, 2 parts of strong hydrochloric acid to 1 of water (not counting the small amount of free sulphuric acid present), the antimony sulphide will redissolve on slight warming, while the arsenic sulphide should be unaffected.

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10. Rowell's Method for Antimony in Ores and Alloys.*—The following method is based on the reaction

$$KBrO_3 + 3SbCl_3 + 6HCl \rightarrow 3SbCl_5 + KBr + 3H_2O.$$

A method based on this reaction was first suggested by Gyory and modified by Nissensen and Siedler for testing hard leads. The present method is a modification of the latter.

Standard Arsenious Chloride Solution.—Into a 500-cc. graduated flask 0.8235 gram of pure powdered arsenious oxide, dried carefully at 100° C., is weighed. About 5 cc. of 10 per cent sodium hydroxide solution are added, and the flask is shaken and gently warmed until the arsenic is completely dissolved; 5 cc. of strong hydrochloric acid are added and the solution is made up to the mark with water. Fifty cubic centimeters of this solution, equivalent to 0.10 gram of antimony,[1] are measured off with a pipette, the delivery of which has been checked against the 500-cc. flask. A solution made in this way and kept in a well-stoppered bottle remains unchanged for a fortnight without oxidation.

The Indicator.—One-tenth of a gram of pure methyl orange is dissolved in 100 cc. of hot water. Drops of this indicator should be taken out with a tube to avoid the stain left about the neck of the

* H. W. Rowell, Jour. Soc. Chem. Ind., XXV, 1181.

bottle, as this or an old solution is liable to leave a stain and spoil the sharp finish. Methyl blue and other methyl colors stable in hydrochloric acid generally stain the solution, while indigo turns green toward the finish, and the end is not so easily distinguished as with methyl orange. More of a solution of indigo is also required to produce a sufficient color, which makes the test a trifle higher.

The Standard Potassium Bromate Solution is approximately N/20, and is made by dissolving 1.41 grams of the "pure" salt in 1 liter of water. The theoretical quantity is 1.3918 grams, per liter,[2] but the "pure" salt always contains bromide which, however, makes no difference to the test. To standardize the solution, 20 cc. of strong hydrochloric acid are added to 50 cc. of the standard arsenic solution, and the mixture brought just to the boil. Thirty cubic centimeters of the bromate solution are then added, and the titration finished in exactly the same way as in the method below, all the precautions being observed. The solution should be standardized every week, as it loses value at the rate of about 2.5 cc. per liter per week.

A one-fifth normal solution may be used for titrating larger quantities of antimony.

Bromine Solution.—Thirty-five cubic centimeters of pure bromine, thoroughly shaken up with 250 cc. of strong hydrochloric acid, makes a saturated solution, and leaves excess of bromine. The required quantity is conveniently measured by dipping in a pipette without any stem below the bulb and so allowing it to fill.

Method of Analysis.—One gram of the finely divided ore or alloy, containing not more than 0.15 gram of antimony, is weighed off into a 500-cc. beaker. These quantities may be varied, provided that more of the substance can be conveniently dissolved, and that the amount of standard bromate solution required is within the compass of the burette used. To the sample, 25 cc. of concentrated hydrochloric acid and 5 cc. of the saturated solution of bromine in hydrochloric acid are added; the covered beaker is then placed on a warm iron plate, so that the temperature is not high enough to drive off the bromine before complete solution is effected, and occasionally shaken until complete solution takes place.

Antimony oxides, and precipitates of mixed oxides of antimony and tin which do not dissolve readily in this way, may be fused with eight times their weight of caustic soda in a silver crucible at a dull-red heat, till the mass turns yellowish-green.[3] The fused mass is dis-

solved in as little water as possible and transferred to a 500-cc. beaker and the solution acidified with hydrochloric acid and evaporated down to 10 cc., when 20 cc. of hydrochloric acid are added. To reduce the antimony, 3 or 4 grams of fresh sodium sulphite crystals are added, the cover and sides of the beaker lightly rinsed down with water, and the liquid evaporated, with the cover on, to 10 cc. or a little less if possible. Although there seems to be little risk of the antimony oxidizing during the evaporation, the cover is better kept on, as it retards the evaporation very little and often saves a test when it, or one near it, spurts through evaporating too far.

Sodium sulphite is better than sulphurous acid for effecting the reduction, as it raises the boiling-point considerably toward the finish and ensures complete volatilization of the arsenic. If more than 2 or 3 per cent of arsenic are present, 20 cc. of strong hydrochloric acid and 5 cc. of saturated sulphurous acid are added, and the liquid boiled down again.

To the concentrated solution, 20 cc. of strong hydrochloric acid and 40 cc. of hot water are added, the cover and sides of the beaker are rinsed, and the whole is boiled for one minute to remove traces of sulphurous acid. The standard solution of potassium bromate is now run in, to within a few cubic centimeters of the necessary amount, with constant and thorough stirring, and at the rate of 30 cc., at most, every fifty seconds.* If lead chloride begins to crystallize, the solution must be boiled again, but otherwise two drops of methyl orange solution are added, and the bromate run in drop by drop, till the color of the indicator is destroyed. The solution should be kept at a minimum temperature of 60° C., and should be thoroughly stirred during the titration so that a local excess of bromate never forms, otherwise some of its value is lost before it attacks the antimony. The result is calculated from the equation

$$\frac{(\text{cc. of bromate required by 1 gram sample} - \text{blank})\ 10}{\text{cc. of bromate required by 50 cc. of arsenic solution}} = \text{per cent Sb.}$$

A blank test should be made occasionally in exactly the same way as above, the sample being omitted, and the result (which should not exceed 0.2 cc.) subtracted from each test.

* A preliminary run on approximately half of the solution, to which methyl orange has been added at the outset, will indicate the approximate end-point. This titrated portion may then be added to the rest and the titration completed carefully.

Possible Sources of Error.—The most probable source of error is the incomplete removal of arsenic or sulphur dioxide.

Oxidation need not be feared if the cover is kept on. The liquid must not be allowed to evaporate to dryness, as antimonious chloride begins to volatilize at about 195° C., and boils at 220° C.

Lead, zinc, tin, silver, chromium and sulphuric acid have no effect upon the test, but large quantities of calcium and ammonium salts tend to make the result high.

Iron tends to make the results high, but not in as great a ratio as copper. Iron is very slightly reduced by sulphurous acid in a strong hydrochloric acid solution, and if, before the sodium sulphite is added to a test, it is boiled down to as small volume as possible and made up again with cold, strong hydrochloric acid, the effect of iron is almost destroyed. With this precaution, 1 per cent of iron raises the test about 0.02 per cent, while 5 per cent has very little more effect.

The Effect of Copper.—Copper is partially reduced by sulphurous acid in a strong hydrochloric acid solution, and, under the conditions of the method given, raises the test in a fairly constant ratio as shown by the following figures:

	Gram Sb.
0.001 gram of copper as cupric chloride in a blank test	=0.0001
0.005 gram of copper as cupric chloride in a blank test	=0.0005
0.010 gram of copper as cupric chloride in a blank test	=0.0012

The quickest and most satisfactory way of obviating the effect of copper is to dissolve the substance in 15 cc. of nitric acid (1 : 2), evaporate just to dryness, and boil for a few minutes with 50 cc. of 1 per cent nitric acid; allow to settle and pour off the liquid through a fine filter. Add 30 cc. of 5 per cent solution of ammonium nitrate, boil again, and transfer all the precipitate to the filter, wash two or three times with a hot 5 per cent solution of ammonium nitrate, and dry the filter and precipitate. Separate the latter from the filter and fuse it and the filter ash together as directed above.[4]

Perhaps as exact a way, when the copper amounts to about 1 per cent, is to subtract 0.012 per cent of antimony for every 0.1 per cent of copper, the copper being estimated by a separate colorimetric test.[5]

By the above method an estimation of antimony in antimonial lead can be carried out in one hour from the time of weighing.

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[1] As_2O_3 when oxidized, is changed to As_2O_5. Thus 2 atoms of oxygen are required for 2 atoms of arsenic. For convenience we may say $As_2 = O_2$, or, $As = O$.

When antimony in the *ous* condition is oxidized, the amount of oxygen required, without regard to the actual combination in which the antimony may occur, whether chloride or otherwise, is the same as though the antimony existed as Sb_2O_3 and were changed to Sb_2O_5. Sb_2O_3 requires O_2 to be changed to Sb_2O_5, or, $Sb_2 = O_2$ and $Sb = O$.

Accordingly, as $As = O$ and $Sb = O$, $As = Sb$. This means that 74.96 parts by weight of As are equivalent to 120.2 parts of Sb.

Now 50 cc. of the arsenic solution contains 0.08235 gram of As_2O_3, equivalent to 0.06237 gram of As. The weight of Sb to which this is equivalent is therefore derived from the proportion $74.96 : 120.2 = 0.0637 : x$. $x = 0.10$ gram.

The original figure, 0.8235, is, of course, derived by working the above relations in the reverse direction.

[2] The formula is $KBrO_3$, the active constituent is oxygen and all of it is used in the reaction. The hydrogen equivalent of O_3 is H_6; therefore, the amount of $KBrO_3$ corresponding to 1 gram-atom of hydrogen is $\frac{1}{6}$ of its molecular weight, in grams, or, 27.836 grams. This quantity, contained in 1 liter, gives the normal solution. The N/20 solution, then should contain 1.3918 grams per liter.

[3] To avoid loss by spattering, observe the precautions described in 6.

[4] The evaporation with dilute nitric acid converts the antimony into insoluble Sb_2O_3, which is filtered off. The filtrate always contains a trace of antimony, which is less soluble in a solution containing ammonium nitrate.

[5] Weigh 0.1 gram of pure copper, dissolve it in nitric acid and dilute the solution to 100 cc. One cubic centimeter = 0.1 per cent copper, on the basis of 1 gram = 100 per cent.

Add an excess of ammonia to the titrated solution, so as to develop any blue color to be produced by copper. Mix and allow any precipitate to settle.

Place some water in a similar beaker, run in a definite amount of the copper solution from a burette, make alkaline with ammonia and dilute the solution to the same bulk as that in the first beaker. By a succession of trials, match the color of the first beaker as closely as possible. Note the amount of copper solution required and calculate the per cent.

The above simple procedure is not expected to give a very exact result, but is probably quite sufficient for the purpose intended.

CHAPTER VI

ARSENIC

For the technical determination of arsenic in ores and metallurgical products, I have found the following method to be perhaps the most generally applicable and reliable (also see 11):

1. **Method for Ores, etc.***—Treat 0.5 gram of the ore precisely as described for antimony in Antimony, 2 and 3. This will result in the arsenic being obtained on the filter as sulphide, the precipitate, flask and delivery tube having been washed with the hydrochloric acid mixture to remove antimony.

2. Using hydrogen sulphide water,† wash off the delivery tube into the flask and then set it aside temporarily. Now wash out the flask six or seven times with hydrogen sulphide water, pouring over the precipitate in the funnel and allowing the filter to drain completely between washes. This is to remove most of the hydrochloric acid. If a very little acid remains it will do no harm. Reject the filtrate.

Place the flask, which may still contain adhering sulphide, under the funnel. Warm about 15 cc. of a 5 per cent solution of sodium hydroxide in a small beaker or wash-bottle. Cleanse the delivery tube, held over the funnel, with a few drops of this and then continue to run the solution very slowly over the precipitate to dissolve it. Use as little as possible (perhaps 10 cc., but more if necessary). Dilute about 5 cc. of the hydroxide solution with about 50 cc. of hot water for washing. Wash the filter six or seven times with this, but endeavor not to get a bulky filtrate, as it has to be boiled away.

Add to the solution in the flask about 2 grams of anhydrous sodium sulphate and 6–7 cc. of strong sulphuric acid.[1] Support the flask over a small free flame and boil down to small bulk; then, with the flask in a holder, run down to a melt, over a strong flame, as in the original decomposition, using the same precautions in the heating and cooling.

Any small amount of hydrochloric acid present is expelled during

* A. H. Low, Jour. Am. Chem. Soc., XXVIII, 1715. Modified.

† It is best to have this slightly acidulated with acetic acid.

the heating before the arsenious sulphide is decomposed, and therefore causes no loss of arsenic by volatilization as chloride.

Add 50 cc. of hot water to the cold residue in the flask, heat to effect solution and then boil for a short time to expel any possible SO_2. Now add 50 cc. of cold water and cool under the tap, to room temperature. Add a few drops of phenolphthalein solution as indicator and make slightly alkaline with 20 per cent sodium hydroxide solution, then reacidify slightly with hydrochloric acid. Cool again, if at all warm. To the cold, *slightly* acid solution, add 3–4 grams, or an excess, of sodium acid carbonate [2] and then a little starch solution. Titrate with standard iodine solution to a permanent blue tinge. When the end of the titration is near, the color produced by the iodine will fade slowly after each addition of a drop. Proceed cautiously at this point until the addition of a single drop produces a permanent blue tinge. Multiply the cubic centimeters of iodine solution used by the percentage value of 1 cc. in arsenic to obtain the result.

3. Standard Iodine Solution.—With 0.5 gram of ore taken for the determination, a convenient strength for the iodine solution is 1 cc. = about 0.5 per cent As.

Dissolve 15 grams of potassium iodide and 8.5 grams of iodine in 20 cc. of water, and make up to 1 liter.

Standardize as follows: Weigh accurately about 0.130 gram of pure, dry, powdered arsenious oxide into an 8-oz. flask and dissolve by warming with 10 cc. of 5 per cent potassium hydroxide solution. Dilute to about 125 cc. with cold water, add a few drops of phenolphthalein solution, and make slightly acid with hydrochloric acid. Cool completely, under the tap. Add 3–4 grams, or an excess, of sodium acid carbonate, then a little starch solution and titrate with the iodine solution to a permanent blue tinge.

Multiply the weight of As_2O_3 taken, by 0.7577, to find the equivalent weight of As.[3] Convert this to percentage value on the half-gram basis (about 22 per cent) and divide this by the number of cubic centimeters used. This gives the percentage value of 1 cc. of the iodine solution in arsenic.

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[1] The arsenic is already in the *ous* condition, as required for the subsequent titration; therefore no reducing agent, such as a piece of filter-paper, is necessary. In any event, the free sulphur present after acidification would serve as a sufficient reducing agent.

[2] Before the sodium acid carbonate is added, the solution contains a slight

excess of hydrochloric acid. The sodium salt neutralizes this, leaving the solution aicd with only CO_2, together with an excess of the acid carbonate. The reaction during the titration may be expressed as follows:

$$H_3AsO_3 + I_2 + H_2O \rightleftarrows H_3AsO_4 + 2HI.$$

The reaction is reversible, the presence of hydrochloric or hydriodic acid tending to make it proceed from right to left. The excess of sodium acid carbonate, which is otherwise without effect, neutralizes the hydriodic acid as fast as it is formed, so that the reaction proceeds completely from left to right. Free alkali is not permissible, as it causes reactions with the iodine.

[3] The above reaction shows that As corresponds to I_2; that is, 74.96 parts by weight of As = 253.84 parts of I. If 1 cc. of the iodine solution contains 0.0085 gram of iodine, we have the proportion $74.96 : 253.84 = x : 0.0085$. This gives $x = 0.00251$ gram, the value of 1 cc. in arsenic, or, about 0.5 per cent on the half-gram basic.

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4. Method for Lead, Copper, Alloys, etc.—It will frequently suffice to take 0.5 gram of the finely divided material and treat it just as described for ores. Or, the method described in ANTIMONY, **9** may be followed, until the arsenious sulphide, free from antimony, is obtained on the filter. From this point follow the directions given in **2**.

5. Pearce's Method Modified.*—Thoroughly mix 0.5 gram of the finely ground ore in a platinum dish or large porcelain crucible, with 5 grams of a mixture of equal parts of dry sodium carbonate and potassium nitrate. It is a good plan to reserve a portion of the mixed salts for use as a cover. Heat the mass gradually over a Bunsen burner to complete fusion. It is best to use a very low flame at first and take plenty of time, so that the mixed salts will melt and soak through the mass before much decomposition occurs; in this way loss of arsenic is prevented with some ores that tend to lose arsenic by volatilization. Finally, heat to the full power of the Bunsen burner until thorough decomposition is effected. Prolonged heating over a blast-lamp is sometimes necessary, especially with oxidized ores containing lead.

6. The melted mass should finally present a smooth and homogeneous appearance if the dish or crucible is taken up in the tongs and given a circular movement. Cool, extract the soluble portion by heating with water until thoroughly disintegrated, and then filter and wash the residue with cold water. Receive the filtrate in an

* This method was originally developed by Dr. Pearce and the author in the laboratory of the Boston and Colorado Smelting Works, at Argo, Colorado.

8-oz. flask. Drop a bit of litmus paper into the flask and then add nitric acid carefully until the solution is plainly acid, simply avoiding a large excess, but if a precipitate has formed always add enough acid to dissolve it. Now add a sufficient quantity, as explained below, of a solution of silver nitrate, which will usually cause a white precipitate of silver chloride, and then cautiously add ammonia until, if arsenic be present, a reddish precipitate of silver arsenate appears. If too much ammonia be added, the precipitate first formed will redissolve and may not be observed at all. In this case the bit of litmus paper in the liquid will show an alkaline reaction. Now cautiously add nitric acid (best dilute) until the red precipitate just redissolves or the litmus paper shows a slight acid reaction. To the faintly acid liquid add a few cubic centimeters of a strong solution of sodium acetate or 1 or 2 grams of the crystals. This will effect a replacement of the free nitric acid, with acetic acid, and all the arsenic will be at once precipitated as silver arsenate, Ag_3AsO_4.

In order to avoid an unnecessarily large excess of silver nitrate, it is best to make up a solution containing, say, 17 grams in 500 cc. and use a definite amount. One cubic centimeter of a solution of this strength will precipitate approximately 0.005 gram of arsenic, or 1 per cent if 0.5 gram of ore is taken for assay. Thus 10 cc. will be an excess in most cases.*

Heat the precipitated mixture to boiling and then cool to room temperature, allowing the precipitate to settle somewhat, and filter. If the first portions run through turbid, return them to the filter once more. Test the filtrate with a little more silver nitrate and sodium acetate. Wash the precipitate with cold water until a portion of the washings shows only a faint cloud when tested for silver with a soluble chloride.

Now place the original flask under the funnel and dissolve the arsenate on the filter with cold dilute (1 : 1) nitric acid; 5 or 10 cc. will usually suffice. Wash the filter thoroughly with cold water. A white residue of silver chloride usually remains undissolved. Dilute the filtrate, if necessary, to about 100 cc., add about 5 cc. of a strong solution of ammonio-ferric alum, and titrate to a permanent red tinge with a solution of ammonium thiocyanate (Volhard), shaking well, especially at the end, to break up the clots of precipitate and free any

* It is best to use at least 10 cc. in every case, as small amounts of arsenic may entirely fail to precipitate unless a considerable excess of silver nitrate be added.

solution held mechanically. Multiply the number of cubic centimeters required, by the arsenic value of 1 cc. to obtain the amount of arsenic in the ore.

7. If the thiocyanate solution contains 7.612 grams of NH_4SCN per liter, 1 cc. will equal 0.0025 gram, or 0.5 per cent, of arsenic.[1] It should be standardized carefully, either against pure silver or silver nitrate, which contains 63.51 per cent of silver. Weigh accurately about 0.5 gram of pure silver, dissolve in a little nitric acid, and dilute to about 100 cc. or, instead, weigh about 0.8 gram of silver nitrate and dissolve in 100 cc. of water acidified slightly with nitric acid. In either case add a few cubic centimeters of a strong solution of ammonio-ferric alum (acidified with a little nitric acid) as an indicator, and titrate to a faint-red tinge with the thiocyanate solution as described above. From the number of cubic centimeters required and the weight of silver taken, determine the value of 1 cc. in silver. The formula of the red precipitate, Ag_3AsO_4, shows that 323.64 parts of silver represent 74.96 parts of arsenic, and, accordingly, the arsenic value of 1 cc. of the thiocyanate solution is easily deduced from the silver value by proportion.[2]

8. In testing heavy sulphide ores there is some danger of a loss of arsenic by volatilization during the deflagration. To avoid this proceed as follows: Cover the dish containing the weighed ore with a watch-glass. Add a little nitric acid and then heat gently, with the cover on, to complete dryness. The dish may be placed above a small free flame and the heat increased at the end. Allow to cool, loosen any spatterings on the cover with a moistened rubber-tipped glass rod, and rinse them into the dish with as little water as possible. It is usually unnecessary to evaporate off this water if the amount is small. Add the 5 grams of nitrate mixture, heat cautiously to dryness, and then fuse and proceed as usual.

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[1] When NH_4SCN precipitates silver, the precipitate formed is AgSCN; that is, 1 molecule of NH_4SCN is required for each atom of silver. This may be expressed as $NH_4SCN = Ag$, or, in grams, 76.113 grams of $NH_4SCN = 107.88$ grams of Ag, from the molecular and atomic weights respectively.

Now the red precipitate of silver arsenate, Ag_3AsO_4, containing all the silver that is to be titrated, shows that every As is represented by Ag_3. $Ag_3 = (NH_4SCN)_3$ therefore, $As = (NH_4SCN)_3$, or, 74.96 parts by weight of $As = 228.34$ parts of NH_4SCN. Thus we obtain the proportion, $228.34 : 74.96 = x : 0.0025$. $x = 0.007612$. This means that 1 cc. of the thiocyanate must contain 0.0076 grams of

the salt, if it is to equal 0.0025 gram, or 0.5 per cent of arsenic, or, 7.612 grams per liter.

[2] 324.64 : 74.96 = Ag value found : As value required.

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9. Sodium Carbonate and Zinc Oxide Method for Ores, etc.*— Thoroughly mix 1 part of dry sodium carbonate and 4 parts of zinc oxide. Weigh 0.5 gram of the ore into a platinum dish and intimately mix it with 3 grams of the above mixture, then cover with 2 grams more. Partially cover the dish with a thin piece of asbestos board, so as to keep in the heat, and heat over a Bunsen burner to bright redness for about twenty minutes. An uncovered porcelain dish may be used, similarly heated in a muffle. Allow to cool and transfer the mass to a suitable beaker, rinsing out the dish with hot water and making up the bulk in the beaker to about 50 cc. Heat the mixture to boiling, stirring well, and filter, washing thoroughly with hot water.† Receive the filtrate in an 8-oz. flask. Drop a small bit of litmus paper into the solution as an indicator and then make slightly acid with acetic acid. Now add an excess of silver nitrate solution, as described in **6**, and agitate the mixture occasionally for a few minutes without heating. Filter the silver arsenate, refiltering if any runs through, and finish the determination as described in **6**.

Note.—For an arsenic determination, where antimony is not also required, this method is shorter and simpler than either of those previously described, but I have found it inapplicable to oxidized ores containing much lead, as some of the arsenic always combines with the lead and fails to be extracted. A determination can easily be made in about fifty minutes. The following test indicates that antimony does not interefere:

An oxidized ore treated by my own methods gave

Arsenic	9.365 per cent
Antimony	0.47 per cent

In trying the above method with this ore, 0.5 gram was weighed into a platinum dish and 0.1 gram of Sb_2O_3 added. This was equivalent to increasing the antimony contents of the ore to about 17 per cent. Two grams of the zinc oxide mixture were intimately mixed with the above and about a gram more was used as a cover. The

* W. C. Ebaugh and C. B. Sprague, Jour. Am. Chem. Soc. XXIX, 1475.

† The arsenic is in the form of soluble sodium arsenate.

dish and contents were kept at a bright red heat over a Bunsen burner for fifteen minutes and the assay then finished as described. Found, arsenic 9.365 per cent, exactly checking my result by the other method.

10. Method of L. L. Krieckhaus.*—Decompose 0.5 gram of the ore with the zinc oxide mixture precisely as described in **9.** Receive the filtrate in an 8-oz. flask and boil it down to 50 cc. After cooling, add 50 cc. of strong hydrochloric acid and again cool. Now add 10 cc. of a 20 per cent potassium iodide solution (the solid salt would fail to dissolve properly in the strong acid) and allow a minute for the reaction to become complete, as follows:

$$H_3AsO_4 + 2HI \rightleftarrows H_3AsO_3 + H_2O + I_2.$$

This reaction can be made to go completely in either direction, according to the conditions.† In the strongly acid solution prescribed, it proceeds from left to right. Now add about 100 cc. of cold water and titrate to complete decolorization with a standard solution of sodium thiosulphate. No indicator is required, as the end-point is easily observed. The thiosulphate solution used in the iodide method for copper (COPPER, 1) may be employed. The copper value multiplied by 0.59 will give the arsenic value.[1]

When the solution of the sintered mass, after the decomposition, is colored green or pink by manganese, add 5 cc. of alcohol or hydrogen peroxide and boil to precipitate the manganese before filtration. Chromium, if present, interferes as in the Pearce method. Phosphorus does not.

I have found this an excellent method. The treatment of the filtrate is simpler than the procedure of Sprague and Ebaugh, and the result quite as accurate. There is the same objection to both methods, however, and that is the difficulty of decomposing oxidized lead ores so as to form a soluble alkali arsenate. Acting on Krieckhaus' idea, I have devised the following method, which appears to overcome this objection and be suitable in all cases, although I have not had the opportunity, as yet, of making many comparative tests.

11. Author's Zinc Oxide Method.—Prepare a mixture of 1 part sodium carbonate, 1 part potassium nitrate, and 2 parts zinc oxide. To 0.5 gram of the ore in a platinum dish add 5 grams of this mixture, and grind intimately together with an agate pestle. Heat the dish

* Eng. and Min. Jour., Vol. 90, 357.

† E. W. Washburn, Jour. Am. Chem. Soc., XXX, 31. (Cf. Note 2 to ARSENIC, **2.**)

and contents gradually to dull redness, then to bright redness for perhaps ten minutes. If a Bunsen burner is used, nearly cover the dish with a piece of thin asbestos board to prevent radiation. A porcelain crucible and muffle heating may be employed if desired. Cool, disintegrate the sintered mass with hot water and filter, washing the residue on the filter six or seven times with hot water. Receive the filtrate in an 8-oz. flask. Add to the filtrate 6 cc. of strong sulphuric acid (this should be an ample excess) and boil to strong sulphuric acid fumes. The final heating is best done over a free flame. Allow to cool, add 50 cc. of water, heat, if necessary, to effect solution, cool again, and add 50 cc. of strong hydrochloric acid. Once more cool the slightly warm solution, add 4 cc. of a 50 per cent solution of potassium iodide (this is the usual solution for the iodide method for copper), mix and allow to stand about a minute. Now add 100 cc. of cold water and titrate with sodium thiosulphate solution as in **10.** It is best to run a blank and deduct for the drop or so of thiosulphate required. Chromium and phosphorus do not interfere, nor does any small amount of manganese that may pass in solution through the filter.

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[1] In the reaction with copper, shown in COPPER, **2**, it will be observed that 2 atoms of copper set free 2 atoms of iodine, which are titrated. That is, $Cu_2 = I_2$, or, $Cu = I$.

In the Krieckhaus method, the reaction given shows that for every atom of arsenic, 2 atoms of iodine are set free to be titrated. That is $As = I_2$.

If $Cu_2 = I_2$ and $As = I_2$, then $Cu_2 = As$, or, with reference to the atomic weights, 127.14 parts by weight of Cu = 74.96 parts of As. This gives 1 part of Cu = 0.5899 parts of As. The figure 0.59, given in the text, is usually sufficiently accurate.

The same figure can be obtained without reference to the reactions quoted, except in a general way. Cupric copper is reduced to cuprous and arsenic in the *ic* condition is reduced to the *ous* condition. The relations between copper and arsenic are precisely the same as though we simply considered the oxides. $2CuO$, or, $Cu_2O_2 = Cu_2O + O$. We may then say, for simplicity, $Cu_2 = O$.

$As_2O_5 = As_2O_3 + O_2$. This gives, in the same way, $As_2 = O_2$, or, $As = O$. We now have $Cu = O$ and $As = O$, therefore, $Cu_2 = As$, which is the same relation we obtained above.

This simple method of reasoning is of general application in volumetric analysis. If we know what happens to the constituents under consideration, the writing out of extended reactions is unnecessary.

CHAPTER VII

BARIUM

1. Method for Ores.—Decompose 0.5 gram of the ore in a 4-oz. Erlenmeyer flask, or a covered beaker, by one of the methods described for **Insoluble Residue** (xxiv), according to its nature. When solution is as complete as possible, add a few drops of strong sulphuric acid to make sure that all the barium will be rendered insoluble. Dilute the mixture with about 50 cc. of water, heat to boiling, and filter, washing with hot water. If the ore contains lead, add about 5 grams of ammonium chloride before boiling and filtering, in order to retain it all in solution.[1] Place the filter and insoluble residue containing the barium in a platinum dish or crucible and ignite to burn off the filter-paper. Mix the cold residue with 3–5 grams of mixed sodium and potassium carbonates[2] and fuse for a short time to convert the barium to carbonate. After cooling, heat the melt with water until disintegration is complete. If a platinum dish has been used it will probably hold sufficient water for the purpose; a platinum crucible may be placed in water in a beaker. Filter, washing with dilute ammonia water[3] until sulphates are all removed. If desired, the filtrate may be tested from time to time by collecting a portion in a test-tube, slightly acidifying with hydrochloric acid, then adding a little barium chloride solution and warming. When no white precipitate of barium sulphate forms the washing is sufficiently complete.

Rinse the more or less impure barium carbonate on the filter, as completely as possible, into a small beaker. Some barium carbonate will still remain on the filter, and there may also be a little adhering in the dish or crucible used for the fusion. Dissolve the latter in 5 cc. of strong hydrochloric acid and then transfer this to the beaker containing the bulk of the carbonate, covering at once with a watch-glass to avoid loss by spattering. Warm the solution, wash off the cover and remove it and then pour the liquid through the filter last used, so

as to dissolve whatever barium carbonate was left there. Wash beaker and filter with hot water and receive the filtrate in a large beaker. Dilute to about 300 cc., heat nearly to boling, and add about 3 cc. of strong sulphuric acid diluted with sufficient water to prevent violent action. Cover the beaker, boil a short time, and then allow to stand until cold, or, best, over night, to insure the complete precipitation of the barium sulphate. Finally filter through a double paper and wash well with hot water. The precipitate is very fine and is liable to run through. The best Swedish or German filters usually give no trouble. It is safest to decant carefully through the filter without disturbing the precipitate in the bottom until most of the clear liquid is gone, then remove the beaker containing the filtrate and replace it with another, so that if the barium sulphate runs through there will be less liquid to refilter. Always rub out the beaker with a rubber-tipped glass rod. The combined filtrate and washings should be allowed to stand, hot, for a while longer, until it is certain that the precipitation is complete. The moist precipitate and filter may be ignited together over a Bunsen burner in a weighed platinum or porcelain crucible. The strong heat of a blast-lamp should not be employed. The carbonaceous matter of the filter may reduce some of the barium sulphate to sulphide, but ignition with free access of air will easily effect reoxidation. The ignited barium sulphate should be perfectly white. The weight of the $BaSO_4$ multiplied by 0.657 will give the corresponding weight of BaO, if the latter is required.[4]

In rapid technical work it is usually sufficient to ignite the barium sulphate in a small clay " annealing-cup," and, when cold, shake and brush it from the cup to the scale-pan for weighing.

In smelter practice the barium is usually required to be reported as sulphate, and all the barium in the ore is considered as existing as sulphate.

2. Short Method.—The following method, though not so reliable, will frequently serve for technical purposes:

Having obtained the insoluble residue, including the barium sulphate as above, ignite it in a small platinum dish to burn off the filter paper, and then, after cooling, add a few cubic centimeters each of strong hydrochloric and hydrofluoric acids, in the order named, and evaporate on the water-bath nearly or quite to dryness. It is best to repeat the operation to insure the complete expulsion of the silicic acid.[5] Finally, take up in hydrochloric acid, dilute with hot water,

and filter. Wash the residue well with hot water and then ignite and weigh as $BaSO_4$ as described above.

3. **Filtering Barium Sulphate.**—I have found it advisable, even with the best papers, to use a double filter.

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[1] The ammonium chloride forms a soluble double salt with the lead sulphate.

[2] The mixed carbonates are used simply because the mixture fuses more easily than either of the single salts. $Na_2CO_3 + BaSO_5 \rightarrow BaCO_3 + Na_2SO_4$.

[3] Barium carbonate is less soluble in water containing ammonia than in pure water.

[4] Molecular weight of $BaSO_4$ is 233.43, that of BaO is 153.37. $153.37/233.43 = 0.657$.

[5] Hydrofluoric acid decomposes silicates, dissolving the silica, which subsequently volatilizes as silicon fluoride, SiF_4.

CHAPTER VIII

BISMUTH

1. Method for Ores, etc.—Treat 0.5 gram of the finely ground ore in an 8-oz. flask with 6–10 cc. of strong nitric acid, and boil gently, nearly to dryness. Add 10 cc. of strong hydrochloric acid, or more if necessary, and warm until solution is as complete as possible. Remove from the heat and add (cautiously) 8 cc. of strong sulphuric acid. With the flask in a holder, boil over a free flame to strong sulphuric acid fumes. Allow to cool.

Add 25 cc. of water and boil gently for a short time to insure solution of all the bismuth sulphate, then cool under the tap and filter, washing with dilute (1 : 10) sulphuric acid. Do not allow to stand long before filtering, or some basic bismuth sulphate may separate.

Dilute the filtrate with about 25 cc. of water and pass in hydrogen sulphide to saturation. Bismuth, copper, arsenic, antimony, etc., are precipitated as sulphides. Filter, washing with hydrogen sulphide water.

Rinse the precipitate as completely as possible into a beaker, add 3–4 grams of pure potassium cyanide and warm gently for some time. Bismuth sulphide will remain undissolved, also cadmium sulphide, if present, and any lead (as sulphide) that may not have been removed as sulphate.

Filter through the same filter as before, in order to act upon the traces of sulphides that could not be washed into the beaker. Wash with hot water.

Spread out the filter on a watch-glass and rinse off the sulphides into a beaker with hot water. To any adhering residue on the filter add a little dilute (1 : 2) nitric acid and warm until dissolved, then rinse into the main portion. Add a little strong nitric acid to the mixture in the beaker, if apparently necessary, and warm until the bismuth is all in solution and the separated sulphur is clean. Dilute somewhat and then filter, washing thoroughly with 1 : 2 nitric acid.

Dilute the filtrate, contained in a large beaker, to about 300 cc. and heat to boiling. Remove from the heat, and, to the hot solution, add dilute ammonia (one-third strong ammonia and two-thirds water) very cautiously, finally drop by drop, until the free acid is neutralized and the liquid remains faintly opalescent. There should not be a visible precipitate, but just a faint cloudiness. If the amount of bismuth is very small, this point may be difficult to observe, in which case drop in a bit of litmus paper, and, working with dilute nitric acid and dilute ammonia, make the solution just faintly alkaline. Now add 1 cc. of dilute hydrochloric acid (1 : 3). The opalescent mixture will clear for an instant, and then, with an appreciable amount of bismuth present, a white crystalline precipitate of bismuth oxychloride, BiOCl, will form.

Maintain the liquid hot, but not boiling, for about an hour, to allow the precipitate to separate and settle; then filter on a weighed Gooch filter and wash thoroughly with hot water.

Dry the residue at 100° C. to constant weight. Multiply the weight by BiOCl found, by 0.8017, to obtain the weight of the bismuth.[1]

2. Instead of precipitating the bismuth as basic chloride, it may, in the absence of lead and cadmium, be precipitated as basic carbonate, as follows:[2]

Partially neutralize the filtrate from the solution of the bismuth sulphide in nitric acid, with ammonia, but without producing any permanent precipitate, then add a solution of ammonium carbonate in slight excess and heat to boiling. Maintain at a nearly boiling temperature for some time, until the bismuth carbonate has settled well; then filter, washing well with hot water.

Dry the precipitate and transfer it as completely as possible from the paper to a small weighed porcelain crucible. Burn the paper carefully and add the ash to the precipitate in the crucible. Ignite the whole at a low red heat, cool, and weigh as Bi_2O_3. Multiply the weight found by 0.8966 to obtain the weight of the bismuth.[3]

A better procedure, if the amount of the precipitate is small, is to dissolve it on the filter with hot dilute nitric acid, receiving the filtrate in a weighed platinum dish. Evaporate the filtrate to dryness, then ignite, gently at first, but finally to bright redness. Weigh as Bi_2O_3, as before.

Also, if the precipitate is large in amount, most of it may, after

drying, be removed to a watch-glass. Dissolve what still adheres to the filter as just described, and evaporate the solution to dryness. Now add the main portion of the precipitate and ignite as before.

The oxidation of the bismuth sulphide by nitric acid may produce some bismuth sulphate, which would cause a slight contamination of the basic bismuth carbonate with basic sulphate, and the latter would fail to be converted to oxide on ignition. The error thus introduced is ordinarily sufficiently small to be negligible in technical work.

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[1] The molecular weight of BiOCl is 259.46. The atomic weight of the contained Bi is 208. This gives the ratio $208/259.46 = 0.8017$.

[2] The formula for basic bismuth carbonate is given as $(BiO)_2CO_3 + \frac{1}{2}H_2O$.

[3] The molecular weight of Bi_2O_3 is 464. The atomic weight of Bi being 208, the two atoms contained in the oxide weigh 416. This gives the ratio $416/464 = 0.8966$.

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3. Electrolytic Method for Ores.—The deposition of an adherent coating of bismuth on a cathode of the size herein described, and under the conditions named, requires that not much more than 0.03 gram of bismuth shall be present. This may be regulated either by the amount of ore taken for assay or by taking only a portion of the final solution of bismuth for electrolysis. The quantity of bismuth present in an ore may be roughly judged by the bulk of the BiS precipitate.

Take 0.5 gram of ore and proceed precisely as described above (1) until the separated bismuth sulphide has been dissolved in dilute nitric acid and the solution filtered, the filtrate being received in an 8-oz. flask. Now add 6–7 cc. of strong sulphuric acid and boil to white fumes over a free flame. Cool, dilute with 25 cc. of water, and boil gently until all the bismuth sulphate is dissolved. No appreciable amount of lead sulphate should be found. Cool, transfer to the proper beaker, and dilute to 100 cc. with cold water. The solution is now ready for electrolysis. The beaker and electrodes may be the same as used for copper, as follows. (See chapter on ELECTROLYSIS.)

Beaker.—Diameter, about 5 cm.; height, about 8–9 cm. Have a mark at the 100-cc. point.

Electrodes.—The cathode is a platinum cylinder 5 cm. long and 2.5 cm. in diameter. This gives a total surface of about 78.5 sq. cm. With a current of 0.6 ampere, $ND_{100} = 0.76$. The weight of this electrode is about 12.5 grams.

The anode is a stout platinum wire with a flat spiral base, the straight portion of the wire rising out of the center of the base at right angles. Its weight is about 8.5 grams. In use the anode is placed within the cathode with the base a little below the lower edge of the cylinder.

Arrange the weighed electrodes in the beaker so that the top of the cylinder projects a little above the surface of the liquid and cover the beaker with the two halves of a split watch-glass. Electrolyze with a current of 0.6–0.7 ampere; electrode tension about 2.7–3 volts. In $1\frac{1}{2}$ hours remove and weigh the cathode. To do this, disconnect and lift it from the beaker, at the same time washing it with a gentle stream of water, and then immerse it in a beaker of water. Lift it from this, wash off the water with alcohol, dry at 100° C., cool, and weigh. Now dissolve off the bismuth with nitric acid and ignite and weigh once more, and then replace in beaker and electrolyze for another half hour, when both electrodes may be removed and weighed. A slight deposit of Bi_2O_5 is usually found on the anode. Calculate this to Bi and add the weight to that of the cathode deposit. It is well to again clean and replace the electrodes and electrolyze for a while longer to be sure of obtaining the last traces of bismuth. Finally, test the exhausted solution with hydrogen sulphide water.

4. In case the bulk of the bismuth sulphide indicates more than 6 per cent bismuth in the ore, proceed as follows: Dilute the filtered nitric acid solution of the bismuth sulphide to 250 cc., adding more acid if a basic salt begins to separate, and then continue the analysis with a suitable aliquot portion. If the percentage of bismuth is approximately known the proper amount of ore may be taken at the outset.

5. **Bismuth in Refined Lead.***—Dissolve 25 grams of the lead, best rolled or hammered out thin and cut into small pieces, in a mixture of 250 cc. of water and 40 cc. of nitric acid of 1.42 sp. gr., using a large covered beaker. Warm gently until all the lead is dissolved, then remove the beaker from the heat and to the hot solution add dilute ammonia ($\frac{1}{3}$ strong ammonia and $\frac{2}{3}$ water), very cautiously, finally drop by drop, until the free acid is neutralized and the liquid remains faintly opalescent. There should not be a visible precipitate but just a faint cloudiness. Now add 1 cc. of dilute hydrochloric acid (1 : 3). The solution will clear for an instant and then, if any considerable

* Ledoux & Co.

amount of bismuth is present, a crystalline precipitate of bismuth oxychloride will form. Again place the beaker over the heat so the liquid will keep hot but not boil. In an hour the bismuth oxychloride, together with a little lead, will have settled. Filter off the precipitate and wash it once or twice with boiling water. In addition to bismuth and lead, the precipitate may contain some antimony, if any appreciable quantity of the latter is present in the sample. Dissolve the precipitate on the filter in a small quantity of hot dilute hydrohcloric acid (1 : 3), wash the filter with hot water and dilute the filtrate with water, taking care not to make the liquid so dilute as to cause a precipitation of the bismuth as basic chloride. Pass hydrogen sulphide into the liquid to precipitate all the bismuth, lead, and antimony as sulphides, filter, wash once with water and twice with warm ammonium sulphide to dissolve the antimony sulphide, and then, after washing once more with water, dissolve the precipitate of bismuth and lead sulphides by placing filter and contents in a small beaker and heating with dilute nitric acid (1 : 4). Boil so as to thoroughly disintegrate the filter-paper and then dilute somewhat with hot water, and filter. Wash the filter well, first with a little warm dilute nitric acid (1 : 4) and then with hot water. Partially neutralize the nitric acid in the filtrate with ammonia, dilute with warm water to a volume of about 300 cc., and then complete the neutralization and add 1 cc. of dilute hydrochloric acid as described above for the original precipitation. The bismuth will now come down as basic chloride free from lead. Filter on a weighed filter or Gooch crucible, wash well with hot water, dry at 100° C., and weigh as BiOCl. This weight multiplied by 0.8017 will give that of the bismuth.

6. In the absence of appreciable amounts of antimony the precipitation by hydrogen sulphide and subsequent washing with ammonium sulphide may be omitted, as only a small portion of whatever antimony is present is precipitated with the bismuth. In this case the first precipitate, containing the bismuth and a little lead, may be at once redissolved on the filter with warm dilute nitric acid (1 : 4) and the precipitation repeated on the filtrate as described. Copper, silver, arsenic, and such amounts of iron as occur in refined lead to not interfere.

7. **Bismuth in Lead "Bullion."**—The determination of bismuth in impure lead or lead bullion may be carried out on the same lines as described for refined lead. From 10 to 25 grams may be taken,

according to the presumed or known nature of the material. Antimony may usually be assumed to be present. Proceed with the determination precisely as described for refined lead (5) up to the point where the bismuth, lead, and antimony sulphides are dissolved in hot dilute nitric acid. Now, instead of finishing the analysis as described, it is best to repeat the whole series of operations once more. In this way the impurities are more certain to be removed and the BiOCl weighed pure.

8. Eakins's Method for Bismuth in Refined Lead.*—In this method for the determination of bismuth in refined lead and lead bullion the bulk of the lead is removed at the outset by precipitation as sulphate from the nitric acid solution. In my laboratory this method has uniformly given low results as compared to those obtained by the method of Ledoux & Co., some of the bismuth apparently being precipitated with the lead. A description of the method is therefore omitted.

9. Volumetric Method for Ores.—The following scheme is based on Miller and Frank's modification of Riderer's method.†

Weigh 0.5 gram of the ore and proceed as in (1) until the washed sulphides of bismuth, etc., are obtained on the filter. Place filter and precipitate in an 8-oz. flask and heat with 5–10 cc. of 1 : 1 nitric acid until the separated sulphur is clean and the filter well disintegrated. Dilute a little and then filter and wash filter thoroughly with a 1 : 2 nitric acid, best with the aid of a filter-pump. To the filtrate add 30 cc. of a cold saturated solution of tartaric acid, then drop in a bit of litmus paper as an indicator and make the solution slightly alkaline with potassium hydroxide. Now add sufficient potassium cyanide solution to dissolve any precipitate that may have formed (except possibly a little bismuth sulphide thrown down by sulphur in the cyanide), and then pass in hydrogen sulphide gas to saturation. Bismuth sulphide is precipitated; copper, arsenic, antimony, etc., remain in solution. Filter and wash with cold water. Dissolve the bismuth sulphide in dilute nitric acid and filter the solution precisely as described above.

10. The filtrate now contains the bismuth as nitrate, together with some free nitric acid. It is best to have the excess of the latter about 5 per cent. Now add a decided excess (3 or 4 times the amount

* Proceedings Colorado Scientific Society, Feb., 1895.

† Jour. Am. Chem. Soc., XXV, 926.

theoretically necessary for combining with all the bismuth) of the ordinary molybdic acid solution used for phosphorus determinations (PHOSPHORUS, 7).[1] There should be no precipitate produced at this point. Then add a few drops of Congo-red solution (made by dissolving 1 part of Congo-red in 100 parts of 30 per cent alcohol) and slowly run in, with stirring, very dilute ammonia from a burette. A white precipitate will form, and finally the indicator will become pink. Next add a few drops of dilute nitric acid, sufficient to change the color to lilac (just neutral). Now dilute, if necessary, to about 200 cc. and heat slowly on a thick asbestos pad, very hot (60° C.), but not to boiling, and stir vigorously. The precipitate of bismuth ammonium molybdate ($BiNH_4(MoO_4)_2$) should coagulate and appear like silver chloride, perhaps colored pink by the indicator. It should not be yellowish. Filter the hot mixture and wash the precipitate thoroughly with a 3 per cent solution of ammonium sulphate.[2] If the above directions are followed, the precipitation will be complete, but if too much nitric acid is added, so that the indicator is turned back to a decided blue color, the precipitate does not collect or filter as well, and the filtrate may contain traces of bismuth. If the precipitate has a yellow color, the results will be unreliable. In such a case, make alkaline with ammonia, then add nitric acid until the precipitate is dissolved, and repeat the neutralization and heating. It is usually unnecessary to add more ammonium molybdate.

11. Make a mixture of 75 cc. of water and 10 cc. of strong sulphuric acid. Place a portion of this in a beaker and rinse the precipitate into it from the filter as completely as possible. When all is dissolved, pour the solution through the filter to dissolve any remaining precipitate, and wash with the remainder of the acidulated water. Receive the filtrate in a beaker. Dilute to about 200 cc. with hot water and pour the hot solution through a reductor, precisely as described in MOLYBDENUM, 4. Follow the directions there given to the end of the titration with standard potassium permanganate solution.

A blank should be run through the reductor. Dilute 10 cc. of sulphuric acid with water and then continue the dilution to 200 cc. with hot water. Run this through the reductor and titrate as before. Note any slight correction thus obtained and deduct it from the regular reading of the burette.

Multiply the Fe value of 1 cc. of the permanganate solution by 0.621 to obtain the Bi value.[3]

[1] The compound that would be formed is bismuth ammonium molybdate, $BiHN_4(MoO_4)_2$. $2MoO_3$ in this compound correspond to Bi, or, considering the atomic weights, 208 parts by weight of Bi = 288 parts of MoO_3. This gives 1 part Bi = 1.385 parts MoO_3.

The molybdic acid solution referred to contains approximately 100 grams of MoO_3 in 200 cc. 1 cc. = 0.05 gram.

0.5 gram of ore was taken for analysis. 1 per cent = 0.005 gram. 1 part of Bi requires, as above, 1.385 parts of MoO_3; therefore 0.005 gram, or 1 per cent, would require 0.00642 gram of MoO_3. This is the theoretical amount required by 1 per cent of Bi in forming the above compound. The text requires three or four times this amount to be used. Four times 0.00642 = 0.02568, or, roughly, 0.025 gram. This is the quantity contained in $\frac{1}{2}$ cc. of the molybdic solution. Accordingly, for every assumed per cent of bismuth in the ore, $\frac{1}{2}$ cc. of the molybdic acid solution should be used.

[2] This is to prevent the precipitate from hydrolyzing and running through the filter.

[3] This is shown as follows: The formula $BiNH_4(MoO_4)_2$ indicates that $Mo_2 = Bi$. In the titration, Mo_2O_3 is oxidized to Mo_2O_6. Therefore, $Mo_2 = O_3$. In the iron titration, $2FeO$, or, Fe_2O_2, is oxidized to Fe_2O_3. Therefore, $Fe_2 = O$, or, $Fe_6 = O_3$. It follows that $Fe_6 = Mo_2 = Bi$. Then, from the atomic weights, 335.04 Fe = 208 Bi, or, 1 part by weight of Fe = 0.621 parts by weight of Bi.

CHAPTER IX

CADMIUM

1. Method for Ores.—To 0.5 gram of the ore in an 8-oz. flask add 10 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid. Boil until any sulphides present are decomposed and the acid is perhaps half expelled. If oxides still remain, continue to heat with addition of hydrochloric acid until solution is as complete as possible. Finally, add about 6 cc. of strong sulphuric acid and boil, best over a free flame, until fuming copiously. Cool, add about 25 cc. of water, heat to boiling, and allow to stand, hot, for a short time, to insure the solution of anhydrous iron sulphate, etc. Then cool, filter off the insoluble residue (including any lead sulphate), and wash with cold dilute sulphuric acid (1 : 10). Dilute the filtrate to about 200 cc., add 10 grams of ammonium sulphate [1] and pass in hydrogen sulphide gas to saturation. Filter off the precipitated sulphides and wash with dilute hydrogen sulphide water slightly acidulated with hydrochloric acid. Rinse the precipitate from the filter into a beaker as completely as possible, using no more water than necessary, place the beaker under the funnel and pour through the filter a strong cold solution of pure potassium cyanide. Agitate the beaker so as to mix the liquids and use no more cyanide solution than necessary to dissolve the soluble copper sulphide, etc., that may be present. If no bismuth or lead is present (any lead should have been practically all removed as sulphate) the cadmium sulphide will now appear yellow or orange.* Filter the mixture through the same filter as before. If it runs through turbid, return it through the filter until clear. Wash well with dilute hydrogen sulphide water. The cadmium sulphide has a tendency to pack on the filter and impede filtration. If possible, wash it loose each time, and the washing will then proceed much more rapidly. If the washed precipitate appears appreciably discolored, indicating bis-

* When precipitated from sulphuric acid solutions, unless very weak in acid, the cadmium sulphide is orange-colored rather than pure yellow.

muth, proceed as in 2, below. If clean and yellow or orange, dissolve it by pouring through the filter hot dilute (1 : 1) hydrochloric acid, using as little as possible. If the volume of the filtrate is not too large, receive it in a large weighed porcelain crucible; otherwise collect it in a beaker and transfer it to the crucible in small portions at a time. Place the crucible and contents on a water-bath and evaporate the solution of cadmium chloride to complete dryness. Now cover the crucible and add a slight excess of dilute sulphuric acid. When spattering has ceased, remove and rinse off the cover and continue the evaporation as far as possible on the water-bath. Finally, remove the excess of sulphuric acid by cautiously heating over a free flame until no more fumes are evolved. Avoid heating higher than necessary. It is best to place the crucible within a larger one fitted inside with an asbestos ring, so that the crucibles do not touch. Or, the crucible may be supported on a clay triangle on a small iron sand-bath containing no sand, so that it just fails to touch the bottom. When the fumes have ceased to come off, cool and weigh the crucible and contents. The cadmium sulphate, $CdSO_4$, should be pure white and soluble in water without residue. Its weight multiplied by 0.5391 will give the weight of the cadmium, from which the percentage may be calculated.[2]

2. If the cadmium sulphide, after treatment with potassium cyanide, appears dark-colored, bismuth or lead (possibly mercury) may be present. Place the moist precipitate and filter in an 8-oz. flask and add 10 cc. of strong hydrochloric acid and the same amount of water. Boil the mixture until the cadmium sulphide is all dissolved, the hydrogen sulphide expelled, and the filter well disintegrated. Any dark insoluble residue apparently free from cadmium may be neglected. Dilute with 25 cc. of hot water and filter, washing thoroughly with hot water. Dilute the filtrate somewhat, add sodium carbonate in slight excess and then 1 or 2 grams of potassium cyanide. Digest for some time at a gentle heat and filter. Wash with cold water. Bismuth and lead remain on the filter as carbonates. Pass hydrogen sulphide through the filtrate, diluted if necessary. This should precipitate pure yellow cadmium sulphide unless mercury is present, which is rarely the case. Filter, wash with hydrogen sulphide water containing several grams of ammonium nitrate (to prevent running through), and then dissolve in hydrochloric acid and finish as described above.

[1] The presence of a large amount of ammonium sulphate is essential for good results in precipitating cadmium with hydrogen sulphide from a sulphuric acid solution.

[2] The molecular weight of $CdSO_4$ is 208.46. This corresponds to a single atom of cadmium, having an atomic weight of 112.4. The ratio, then, is $112.4 \div 208.46 = 0.5391$.

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3. Electrolytic Method. — Cadmium can be separated electrolytically in a satisfactory manner from its solution in various electrolytes. Its alkaline double-cyanide solution is perhaps as good as any, if not the best electrolyte. The method may be applied to an ore as follows:

4. Treat 1 gram of the ore by the methods previously described until a solution of the chloride or sulphate is obtained, free from the other members of the hydrogen sulphide group. The solution should be evaporated if necessary, so as to have the volume well below 100 cc. Add a drop or two of phenolphthalein solution and then pure sodium or potassium hydroxide solution until a permanent red color is obtained. Now add cautiously a strong solution of pure potassium cyanide until the precipitated cadmium hydroxide is completely dissolved, avoiding an excess. Dilute to 100–125 cc. and, using the same beaker and electrodes as for copper (COPPER, **15**), electrolyze with a current of $ND_{100} = 0.04$ to 0.06 A. and V. = 2.9–3.2. Keep the solution at a temperature of about 60° C. In four to six hours the deposition is usually complete. Test by raising the level of the liquid slightly and noting if any deposition occurs on the clean platinum surface during half an hour or so. When the operation is ended, disconnect and remove the electrode, wash it with hot water, then with alcohol, and finally dry it at 100° C., cool, and weigh.

It is a good plan to replace the electrode in the solution and electrolyze for another half hour. The electrode should first be cleaned with nitric acid, then washed, ignited, and again weighed. If desired, the solution can be tested with hydrogen sulphide. As this may produce a yellow color in the cyanide solution, even in the absence of cadmium, it is best to first acidify with hydrochloric acid (under a hood) and then heat until all the hydrocyanic acid is expelled.

5. Treadwell,* using the same electrolyte, recommends electrolyzing in the cold for five to six hours with a current of 0.5–0.7 ampere

* Treadwell's Analytical Chemistry (Hall), II, 2d Ed., p. 166.

and an electromotive force of 4.8–5 volts. At the end of this time the current is increased to from 1–1.2 amperes and the solution is electrolyzed for one hour more. Treadwell states that unless the current is increased toward the end of the operation, the cadmium will not be all deposited at the end of twelve hours. If the stronger current is used from the beginning, some of the metal is liable to be deposited in a spongy form, resulting in a possible loss in washing.

6. Smith * describes the deposition of cadmium from its sulphate solution. The neutral solution is acidified with 3 cc. of sulphuric acid of 1.09 sp. gr. and diluted to 125 cc. Lily G. Kollock † found that with such a solution, maintained at 65° C., with $ND_{100} = 0.078$ ampere and volts = 2.61, the deposition was complete in five hours.‡

7. Cadmium in Ores and Flue Dust.—(Method of Omaha Plant of Am. Sm. & Ref. Co.)—Treat the material as in 1 until after the first filtration. If the filtrate is likely to contain any copper or bismuth, boil with sufficient sodium thiosulphate to precipitate them as sulphides and filter, washing with hot water. Neutralize the filtrate with ammonia and then reacidify with sulphuric acid to an excess of about 1 cc. of the strong acid. Dilute to about 100 cc., or, if the bulk of the filtrate already somewhat exceeds this volume, dilute to 200 cc. and add an additional cubic centimeter of sulphuric acid. Now heat to boiling and pass in hydrogen sulphide to saturation. Filter, washing precipitate with hydrogen sulphide water. (The filtrate may be analyzed for zinc by boiling off the hydrogen sulphide, oxidizing the iron with a little nitric acid, adding 10 grams of ammonium chloride and continuing according to the "Alternate Method" as described under Zinc.) Wash the precipitated cadmium sulphide off the paper into the original beaker with dilute hydrochloric acid. Add 5 cc. hydrochloric acid and boil.

Continue by either of the following procedures:

A. As soon as the cadmium sulphide is in solution, filter off the insoluble arsenious sulphide. Neutralize the filtrate with ammonia and then just bring it back with hydrochloric acid. Titrate hot with the usual standard potassium ferrocyanide, precisely as for zinc. Standardize the solution for cadmium against C. P. cadmium sulphate.

B. Boil until the solution is reduced to a volume of about 10 cc.

* Electrochemical Analysis.

† Jour. Am. Chem. Soc., XXI, 925.

‡ See Edgar F. Smith's Electro-Analysis for rapid method, using rotating electrode.

Filter into a weighed platinum shell and then evaporate cautiously almost to dryness. Add ½ cc. of strong sulphuric acid and continue heating until fuming strongly. Now continue the heating cautiously until the fuming ceases. Finally increase the heat to low redness for about four minutes. Avoid overheating. Cool and weigh as cadmium sulphate.

8. Cadmium in Spelter.*—Dissolve 25 grams of the sample in a No. 4 beaker in a mixture of 34 cc. of strong sulphuric acid and 250 cc. of water. In the case of very pure zinc it may be necessary to add a few drops of very dilute platinum chloride solution from time to time, to hasten the action. The above amount of acid is approximately 12.5 cc. more than is required to dissolve 25 grams of zinc, and therefore about 12.5 cc. of free acid will remain in the solution. Lead, copper and probably a small amount of cadmium remain undissolved. Pay no attention to the flocculent residue, but be sure that all the zinc is dissolved.

9. Add 15 grams of solid ammonium sulphate to the warm liquid, and pass in hydrogen sulphide for ten minutes.† Allow to stand, warm, for half an hour and then again pass in hydrogen sulphide for ten minutes more. All the cadmium will be precipitated as sulphide, which will be mixed with considerable zinc sulphide, together with lead and copper. Filter through a 12.5-cm. paper and wash three or four times with warm water. The filtration is rather slow but proceeds steadily enough if a good column is established in the funnel stem. Return the precipitate, paper and all, to the beaker in which the precipitation was made, add 10 cc. of strong sulphuric acid and 10 cc. of strong nitric acid. Cover the beaker and heat it until sulphuric acid fumes are given off. Remove the beaker from the source of heat and to the hot, but not strongly fuming, liquid add a few more cubic centimeters of strong nitric acid. Again boil to fumes.

Repeat the addition of nitric acid as above, until the paper is completely consumed. This usually requires about three additions of the acid with intermediate fuming, the whole operation taking about three-quarters of an hour. It is important that the paper be completely oxidized.

10. Cool the solution, dilute to 200 cc. with cold water, then boil, cool and allow to stand until the lead sulphate settles. Filter off the

* Ledoux & Co., N. Y.

† Cf. Notes to 1.

lead sulphate and wash it once or twice with dilute sulphuric acid (1 : 20). The liquid now contains about 10 cc. of sulphuric acid in 200 cc. Add 10 grams of ammonium sulphate and pass hydrogen sulphide into the warm solution exactly as before. Cadmium comes down as sulphide practically free from zinc. Filter through a 9-cm. paper and wash the precipitate three or four times with warm water.

11. Treat paper and precipitate in a No. 2 beaker with 5 cc. of sulphuric acid and 5 cc. of nitric acid, evaporating to fumes. Add nitric acid as before to the hot liquid, and again evaporate, repeating this procedure until the paper is destroyed. Now cool, add 5 cc. of cold water and evaporate to fumes. Do this a second time. These last evaporations are to make certain of the expulsion of all nitric acid. The work should be done in a place free from heavy nitric fumes, since the presence of even a trace of nitric acid in the solution interferes with the subsequent electrolysis of the cadmium.

12. Add 25 or 30 cc. of water to the sulphuric acid residue, and heat until all soluble salts are dissolved. Cool, neutralize the excess of free sulphuric acid with ammonia (using litmus paper as an indicator) and then add 4.5 cc. of 1 : 2 sulphuric acid. This gives a solution containing 1.5 cc. of free sulphuric acid. Dilute with water to 125 cc. and electrolyze (preferably overnight) using a current of 0.1 ampere, 2.6 volts, to about 10 sq. in. of cathode surface (one side). The cathodes are perforated platinum cylinders, $2\frac{1}{8}$ in. high by $1\frac{1}{2}$ in. in diameter. Under the conditions given, cadmium is precipitated free from zinc, even if a trace of zinc remains in the solution. Copper also comes down with the cadmium. After weighing the cathode, dissolve the deposited metal in a few drops of nitric acid, dilute, boil, cool and make alkaline with ammonia. Dilute to 10 cc. and compare the color with a similar solution containing a known amount of copper. The two or three tenths of a milligram of copper usually present may be closely estimated in this way.

13. If the laboratory is not equipped with electrolytic apparatus, cadmium may be determined by weighing as sulphate. Since two precipitations with hydrogen sulphide, as described above, may not remove all the zinc (and will not unless the work is done with great care), a third precipitation with hydrogen sulphide should be made. This is unnecessary when the electrolytic method is used, because under the conditions given a small amount of zinc will remain in the electrolyte.

Wash the cadmium sulphide from the third precipitation with warm water, and then dissolve it in hot dilute nitric acid. Evaporate the solution to smaller bulk, cool, if necessary, and add 0.5 to 1 cc. of sulphuric acid. Evaporate to dryness in a weighed porcelain crucible, and finally ignite at a low temperature to constant weight. The resulting $CdSO_4$ is likely to contain copper. The copper should be estimated colorimetrically, calculated to $CuSO_4$ and deducted.*

Note that the presence of a large amount of ammonium sulphate is essential to good results in precipitating cadmium with hydrogen sulphide from sulphuric acid solutions. The proportions of acid and water are also important in getting clean separations. Those given above should be strictly adhered to.

* The amount of copper present will probably not exceed two or three tenths of a milligram. Dissolve the residue in the crucible by warming with a little nitric acid, transfer the solution to a test-tube, make ammoniacal to develop the blue color due to copper, and dilute to about 10 cc. Prepare a copper solution of known strength as follows: Dissolve exactly 100 mg. of pure copper foil in nitric acid, dilute somewhat, add an excess of ammonia and then make the solution up to 100 cc. 1 cc. = 1 mg. of copper.

From a burette, run some of this solution, say 1 cc., into a test-tube similar to the first. Dilute to the same height as the liquid in the first test-tube and compare the color. Repeat the test with different amounts of the prepared copper solution, until the color of the first test-tube is matched. From the amount of the prepared copper solution required, calculate the copper used. Calculate this to $CuSO_4$ and deduct the weight from the weight of the impure $CdSO_4$ before calculating the Cd.

Example.—Suppose 1.8 cc. of the prepared copper solution were used. This = 0.0018 gram of copper. Atomic wt. of Cu = 63.57. Mol. wt. of $CuSO_4$ = 159.63. Now use the proportion $63.57 : 159.63 = 0.0018 : x$. $x = 0.00452$. This is the weight of $CuSO_4$ corresponding to 0.0018 gram of Cu. Deduct this from the weight of the $CdSO_4$, as found, and calculate the balance to Cd. See note to CADMIUM 1.

By igniting at a very low temperature the copper sulphate present is simply dehydrated, leaving $CuSO_4$. At a high temperature this would be changed to CuO.

CHAPTER X

CALCIUM

1. Ores, etc.—The calcium is usually required as CaO. Treat 0.5 gram of the ore in an 8-oz. flask with whatever acids are best suited to decompose it. Begin ordinarily with 10 cc. of strong hydrochloric acid and heat gently. If sulphides are present, add 5 cc. of strong nitric acid (after the oxides are dissolved) and boil gently until decomposed. If the decomposition is perfect, sulphuric acid is unnecessary, but with ores I usually add 5 cc. at this stage. In any case, boil until most of the free acid is expelled, over a free flame if sulphuric acid has been used. Allow to cool, if necessary, add about 100 cc. of water and 5 cc. of strong hydrochloric acid, heat until the salts are dissolved and then filter (never omit this if there is any appreciable amount of insoluble residue), washing with hot water. To the filtrate add 2 cc. of a saturated solution of potassium dichromate (this may be omitted if lead is absent *), 15–20 cc. of saturated bromine water (to precipitate manganese), and then a very slight excess of ammonia.[1] Cover the beaker and boil until all free ammonia is expelled. Allow to settle somewhat and then filter through an 11-cm. filter and wash thoroughly with hot, dilute ammonium chloride solution[2] (5 grams to 500 cc.). If lead chromate runs through, return the first portions. If the precipitate shows much manganese[3] it is always well to test the filtrate by adding more bromine water and ammonia and boiling a short time. If any manganese comes down, filter it off, it being usually unnecessary to expel the excess of ammonia as before. Wash with the dilute ammonium chloride solution.

The above procedure renders the usual double precipitation of the iron entirely unnecessary. The usual retention of lime by iron appears to be due to the formation of calcium carbonate, by the

* Lead unquestionably interferes, although but slightly. An ore containing 30 per cent lead and about 16 per cent CaO gave results about 0.25 per cent high when the lead was not removed. Lead may also be removed as sulphide, as described in MAGNESIUM, 1.

absorption of carbon dioxide from the air in the presence of free ammonia, and this does not occur if the ammonia is expelled previous to filtration. A neglect to filter off the insoluble residue before the iron precipitation will usually produce a low result. I am unable to state the reason.

2. Make the filtrate from the iron strongly ammoniacal, heat to boiling and add an excess of ammonium oxalate solution. This should be added in sufficient amount to convert all possible calcium and magnesium to oxalates (the magnesium oxalate remaining in solution). Thirty cubic centimeters of a saturated solution should be sufficient in any case. It is best to dilute it somewhat and add it boiling hot. Boil the mixture about ten minutes, allow to stand hot and settle, and then filter through an 11-cm. filter and wash ten times with hot water. For more exact work allow to stand overnight.

The mode of procedure now depends upon whether the ore contains much or little magnesium. In the former case the calcium oxalate is almost sure to contain an appreciable amount of magnesium oxalate and should therefore be purified. Unless the amount of magnesium is known to be insignificant, it is always safest to proceed as follows:

3. Without troubling to wash the precipitated oxalate more than once, rinse it from the filter into a beaker. What little remains adhering to the filter may usually be neglected if the same filter be employed for the next filtration of the oxalate. Heat the mixture in the beaker and then dissolve the oxalates by the addition of as little hydrochloric acid as possible. Dilute to about 50 cc. with hot water, make alkaline with ammonia, and add about 10 cc. of the ammonium oxalate solution. Boil the mixture for about ten minutes, allow to stand, hot, until settled, and then filter through the last filter. Wash at least ten times with hot water, to remove every trace of ammonium oxalate.

When little or no magnesium is present, the first precipitate of calcium oxalate will be sufficiently pure and will require only thorough washing with hot water.*

4. In a 400-cc. beaker prepare a mixture of 5–7 cc. of strong sulphuric acid and about 125 cc. of water. Drop the filter and precipitate into this and heat to about 70° C. Stir to effect the decomposition of the calcium oxalate, but avoid disintegrating the filter. Titrate the hot solution with standard potassium permanganate solution. Under the conditions named, the filter-paper will exercise

* This is the usual practice in all cases in ordinary lead-smelter work.

practically no influence on the result, and while the final pink tinge will gradually fade, there will be no difficulty in noting a sharp end-point. Multiply the number of cubic centimeters of permanganate required, by the percentage value in CaO of 1 cc. to obtain the per cent of CaO in the ore.

5. The permanganate solution used for iron determinations (IRON, 2) will serve for this titration. The iron factor multiplied by 0.5023 will give the CaO factor. This is because the same amount of oxygen from the permanganate is required to oxidize the oxalic acid in the calcium oxalate corresponding to 1 mol of CaO, as is required to oxidize 2Fe from the ferrous to the ferric condition. That is, 2Fe are equivalent to 1 CaO or 111.68 parts of Fe to 56.07 parts of CaO, which is the same as 1 part Fe to 0.5023 part CaO.[4]

6. For the CaO determination, however, it is best to standardize the permanganate directly against pure oxalic acid.* Weigh about 0.2 gram of the crystals and dissolve in an 8-oz. flask in a previously prepared mixture of 5–7 cc. of strong sulphuric acid and 125 cc. of water. Heat to about 70° C. and titrate to a faint pink tinge with the permanganate solution. The first portion of permanganate will not be decolorized instantly, but when once the decolorization has begun, it will thereafter occur quickly until the end.

Divide the weight of oxalic acid taken by the number of cubic centimeters required. This will give the oxalic acid value of 1 cc. of the permanganate. Multiply this figure by 0.4444 to obtain the value of 1 cc. in CaO, expressed in grams. This last factor is obtained as follows: 56.07 parts of CaO require 126.148 parts of crystallized oxalic acid to form calcium oxalate. Accordingly, 1 part of oxalic acid is equivalent to 0.4444 part of CaO. Of course, in the CaO determination, all the oxalic acid titrated is derived from the decomposition of the calcium oxalate by the sulphuric acid.

Having determined the value of 1 cc. in grams of CaO, the percentage value on the basis of 0.5 gram of ore taken is easily calculated.

Example.—Took 0.2163 gram of oxalic acid. Used 38.66 cc. of permanganate. $0.2163 \div 38.66 = 0.005594$. This is the weight of oxalic acid to which 1 cc. of the permanganate is equal. Multiplying

* Sorenson's Salt (sodium oxalate, $Na_2C_2O_4$) is to be preferred to oxalic acid, because its purity is probably greater. Mol. wt. oxalic acid, $H_2C_2O_4 \cdot 2H_2O = 126.058$. $Na_2C_2O_4 = 134.01$. 1.063 Sorensen's Salt = 1 oxalic acid. $Na_2C_2O_4$ multiplied by $0.4184 = CaO$. Personally, I have found C. P. oxalic acid to be more reliable than the usual "C. P." sodium oxalate.

by 0.4444, we have 0.002486, the value of 1 cc. in grams of CaO, or 1 cc. = 0.4972 per cent on the basis of 0.5 gram of ore taken.

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[1] Bromine is an oxidizing agent. Manganous salts in neutral, ammoniacal or acetic acid solutions are oxidized by it to form MnO_2, which, being insoluble under these conditions, is precipitated. $MnO + 2Br + H_2O \rightleftarrows MnO_2 + 2HBr$.

[2] Ammonium chloride is used to render any calcium carbonate, which may be present, more soluble. Calcium carbonate might be formed either from ammonium carbonate present in the ammonia used, or by the absorption of carbon dioxide from the air.

[3] Indicated by the precipitate, if bulky, being of a much deeper brown than the color of pure ferric hydroxide.

[4] The formula for calcium oxalate is CaC_2O_4. H_2SO_4 acts on this to form $CaSO_4$ and set free oxalic acid, $H_2C_2O_4$. The permanganate oxidizes this to form carbon dioxide and water: $H_2C_2O_4 + O \rightarrow 2CO_2 + H_2O$. 1 Ca, corresponding to CaO, is combined in 1 calcium oxalate, equivalent to 1 oxalic acid. 1 oxalic acid requires 1 oxygen, as above. Therefore, O = CaO.

In the oxidation of iron 2FeO, or Fe_2O_2, $+O = Fe_2O_3$. Then O = 2Fe. Accordingly, $Fe_2 = CaO$, or 111.68 Fe = 56.07 CaO.

This gives Fe, multiplied by 0.5023 = CaO.

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7. Silicates and Substances Not Decomposed by Acids.—These are decomposed, as described under Silica, either by immediate fusion with alkali carbonate or by acid treatment, followed by fusion of the insoluble residue. The nature of the substance will determine these points precisely as in the case of silica. When the solution eventually obtained contains considerable silicic acid, it is best to render it insoluble by evaporation and filter it off. A small amount of silicic acid may be neglected. The clear hydrochloric acid solution finally obtained, containing all the calcium, is treated as described above (1).

8. "Available Lime" in Ores Containing Calcium Fluoride.—Some of the western smelters regard the calcium contained in calcium fluoride as of no value as a flux, claiming that it passes through the furnaces unaltered, without combining with the fluxes used. In paying for the lime in an ore, only that which is not combined with fluorine is taken into consideration and is called "available lime." The method used for determining this portion is not strictly correct, since if an ore contained much calcium sulphate or silicate, at least some of the CaO thus combined would probably fail to be reported as "available." As a technical method, however, in regular use, it is sufficiently satisfactory and is therefore given herewith.

9. Take 0.5 gram of the ore in an 8-oz. flask, moisten with water, add 5 cc. of 80 per cent acetic acid, and boil nearly to pastiness. Take up in about 30 cc. of equal parts of 80 per cent acetic acid and water and boil gently for a few minutes. To remove lead, which is frequently present, add 2 cc. of a saturated solution of potassium dichromate just previous to this last boiling. Filter, washing with hot water. To the filtrate add about 20 cc. of saturated bromine water and then (cautiously) make alkaline with ammonia and heat to boiling. It is generally best to now add more bromine water and continue the heating for a short time to make sure of the precipitation of all manganese. Finally, boil off all the free ammonia, allow to settle somewhat, and filter and wash as in the regular method (1). Test the filtrate for unprecipitated manganese if apparently necessary, as described for the regular method. Make the final filtrate strongly ammoniacal, heat to boiling, precipitate the calcium as oxalate, and finish the determination exactly as described for the regular method.

This will give all the CaO contained in the ore as carbonate and also as sulphate, unless the latter is in large amount. Calcium combined as fluoride or silicate remains practically undissolved by the acetic acid. The silicate is usually small in amount and the calcium so combined is, in fact, regarded as no more "available" than that existing as fluoride.

10. **The Percentage of Calcium Fluoride** may be determined with fair accuracy as follows: Place about 3 grams of powdered anhydrous sodium sulphate in a small platinum dish, mixing in also a little potassium nitrate, if reducible metals are likely to be present. Lay the filter and residue from the above acetic acid treatment upon this mixture, and ignite gently until the paper is fairly well burned off. Now cool and add 5–6 cc. of strong sulphuric acid. Heat carefully, to avoid spattering, first to strong fumes, and then to a melt, if possible. If the mass solidifies at the end, without melting, cool sufficiently, add a little more sulphuric acid and heat again. This will usually effect complete decomposition of the fluoride, even if the mass is not completely melted. Allow to cool, cover the dish and dissolve the cake by warming with sufficient water, acidulated with 5 cc. of hydrochloric acid. Transfer the solution to the original flask, first filtering, if there is an appreciable amount of insoluble residue. Dilute to about 150 cc. with hot water, and proceed with the usualde termination of CaO as described in 1, at the same point. Multiply the

percentage of CaO found by 1.393 to obtain the percentage of CaF_2.

11. **Rapid Volumetric Determination of CaO in Limestone, Cement, Lime, Blast-furnace Slags, etc.***—The following rapid method for the determination of CaO is applicable to materials in which the calcium is present either as oxide, carbonate, or silicate, and is dependent on the fact that calcium can be completely precipitated as oxalate in solutions containing free oxalic acid, while iron, aluminum, and magnesium cannot.

12. **Decomposition of the Sample.**—For high-grade *limestones*, that is, those which when burned do not give a hydraulic lime, weigh 0.5 gram into a platinum crucible, cover and ignite for five minutes over a Bunsen burner, and then for five minutes over the blast-lamp. This heating must be cautiously carrried out, as magnesian stones are likely to fly out if heat is applied too suddenly. Start the ignition over a low Bunsen flame and gradually raise until the full heat is attained, then continue for five minutes and follow with a blast-lamp. Empty the contents of the crucible into a 500-cc. beaker and add 40 cc. of dilute (1 : 1) hydrochloric acid; heat, and when solution of the sample is complete proceed as in **13**.

For *cement rock* or *hydraulic limestones*, weigh the sample as before and carefully mix with it $\frac{1}{4}$ gram of finely ground sodium carbonate, by stirring with a glass rod. Brush off the rod into the crucible and ignite over a Bunsen burner, starting with a low flame and gradually raising it until the full heat is attained. Continue heating for five minutes longer and then ignite over the blast for the same length of time. Place the crucible in a 500-cc. beaker and decompose the sintered mass in the crucible with 40 cc. of dilute (1 : 4) hydrochloric acid, keeping the beaker covered to avoid loss by effervescence. Heat until solution is complete and proceed as in **13**.

For *cement*, pass the sample through a 100-mesh screen, weigh 0.5 gram into a dry 500-cc. beaker and add, with constant stirring, 20 cc. of water. Break up the lumps, and when all the sample is in suspension except the heavier particles, add 20 cc. of dilute (1 : 1) hydrochloric acid and heat until solution is complete. This usually takes five or ten minutes. Proceed as in **13**.

Many *slags* are soluble in concentrated hydrochloric acid. When this is the case, weigh 0.5 gram into a 500-cc. beaker, stir up with a

* From paper by Richard K. Meade, Chemical Engineer, Vol. 1, p. 20.

very little water and add 20 cc. of strong hydrochloric acid and heat. When solution is complete, proceed as in **13**.

13. The Determination.—Carefully add dilute ammonia (sp. gr. 0.96) to the solution of the sample until a slight permanent precipitate forms. Heat to boiling and add 10 cc. of a 10 per cent solution of oxalic acid. Stir until the iron and aluminum hydroxides are entirely dissolved and only a slight precipitate of calcium oxalate remains. Now add 200 cc. of boiling water and sufficient (20 cc.) saturated solution of ammonium oxalate to precipitate the calcium. Boil and stir for a few moments, remove from the heat, allow the precipitate to settle, and filter on an 11-cm. filter. Wash the precipitate and paper ten times with hot water, using not more than 10 or 15 cc. of water each time. Remove the filter from the funnel, open and lay against the sides of the beaker in which the precipitation was made, wash from the paper into the beaker with hot water, add dilute sulphuric acid (4), fold the paper over and allow to remain against the walls of the beaker. Heat to 80° C. and titrate with standard potassium permanganate (5) until a pink color is obtained; now drop in the filter-paper, stir until the color is discharged, and finish the titration carefully, drop by drop.

14. The permanganate is best standardized for this determination by means of pure calcite or Iceland spar, as this does away with uncertain factors and also with the error introduced by the solubility of calcium oxalate. The procedure, which is as follows, is that recommended by the Committee of the Lehigh Valley Section of the American Chemical Society:

Make up potassium permanganate solution by taking 6 grams of the salt to 1 liter of water; let stand a few days before standardizing.

Weigh out 0.5 gram of powdered calcite into a 400-cc. beaker; add 100 cc. of water and 10 cc. of hydrochloric acid (1 : 1); boil gently until all carbon dioxide is expelled, and when completely dissolved make alkaline with ammonia and add, little by little, 20 cc. of boiling-hot saturated solution of ammonium oxalate; continue boiling for five minutes; let settle, filter, wash, transfer precipitate to original beaker (13); dissolve in dilute sulphuric acid and titrate with the permanganate as in the determination of calcium.

15. Note on the Foregoing Method.—In this method lead appears to interfere more or less, bringing the results high; it is therefore not so suitable for ores in general as the longer method first given.

CHAPTER XI

CHLORINE

1. Mohr's Volumetric Method.—The chloride solution should be cold and neutral. If acid, it should be neutralized with pure sodium or calcium carbonate in slight excess. To the cold neutral, or faintly alkaline solution contained in a porcelain casserole or evaporating-dish add 1 cc. of a 2 per cent solution of neutral potassium chromate. Titrate with a N/10 solution of silver nitrate until a permanent faint-red tinge is obtained, due to the formation of silver chromate. This compound cannot exist permanently in the mixture until all the chlorine has been precipitated as silver chloride. The mixture should be well stirred after each addition of silver nitrate, which toward the last should be added only drop by drop. As the faint reddish tinge is somewhat difficult to distinguish, various schemes have been proposed to facilitate its detection. I have found it a good plan, when the end-point is apparently attained, after reading the burette, to pour off half the liquid into a similar casserole and then add 1 more drop of the silver nitrate solution to one casserole and note if the two portions of the liquid now show any difference. When such a difference can be detected, the end-point has certainly been reached and it is usually safe to accept the reading of the burette taken previous to the last drop. For accurate work a blank test should be made on the same volume of liquid to see how much silver solution is required to produce a tint when no chloride is present, and this amount must be deducted from that used in the analysis. Multiply the number of cubic centimeters used, by 0.003545, to obtain the weight of the chlorine present, or by 0.00585 for the weight of the corresponding sodium chloride.

2. The standard N/10 silver nitrate solution for the above titration may be prepared as follows: Heat pure silver nitrate to 120° C. for ten minutes, then cool and weigh 16.994 grams, dissolve in water and dilute to 1 liter. One cc. =0.003545 gram of chlorine, or 0.00585 gram

of sodium chloride. Of course, any other weight of silver nitrate can be taken, and the corresponding value of the solution obtained by calculation.

3. Chlorine in Salts and Liquids Containing Organic Matter and Sulphides.—*Solutions Required*: 1/10 normal silver nitrate. Approximately 1/10 normal ammonium thiocyanate. For ammonium thiocyanate take 8 grams per liter; or, for potassium thiocyanate, take 10 grams per liter. Standardize the thiocyanate against the silver solution, as described below, to obtain the value of 1 cc. in silver solution.

Indicator solution of ferric ammonium sulphate. Make a strong solution and add sufficient nitric acid to remove most of the brown color.

Procedure: Take 200 mg. of the salt, or an equivalent amount of the liquid. Place in an 8-oz. flask and dilute to about 50–75 cc. Add dilute nitric acid in moderate excess and boil a minute or two. Now run in the silver solution from a burette until sure of a slight excess, and then boil the mixture until the silver chloride settles well on short standing. Cool completely, add a few cubic centimeters of the ferric indicator, and titrate with the thiocyanate solution to a faint brownish tint. Note the amount of thiocyanate used, calculate its value in silver solution and deduct this from the amount of silver solution used. The remaining silver solution is the amount required to form silver chloride with the chlorine in the salt or liquid taken, and from this all necessary calculations can be made, as in **1**.

In standardizing the thiocyanate, simply run 25–30 cc. of the silver solution into a flask, dilute to about 75 cc., add some ferric indicator and titrate in the cold to a faint color, shaking well, especially toward the end, after each addition of thiocyanate.

Precipitated AgCl does not interfere with the thiocyanate titration if it has been well coagulated by boiling. If allowed to remain in an opalescent or cloudy condition it will quickly decompose the slight excess of thiocyanate that causes the end-reaction color. The color will disappear repeatedly as more thiocyanate is added and will prevent a correct determination of the end-point. This is because silver thiocyanate is more insoluble than silver chloride.

CHAPTER XII

CHROMIUM

METHODS are given below for the determination of chromium in iron ores, chrome-iron ore, and steel. These will include most of the cases likely to be met by the metallurgical chemist.

1. Method for Iron Ores with Small Amounts of Chromium.*—Fuse 1 gram of the very finely ground ore with a mixture of 5 grams of sodium carbonate and 0.5 gram of potassium nitrate in a platinum crucible or small dish. After fusion, extract the melt with hot water and transfer the mixture to a small beaker. If the solution is colored by manganese, add a little alcohol and warm the mixture. This will precipitate the manganese as dioxide. Allow the precipitate to settle and note the color of the clear solution. If chromium is present it will be more or less yellow. If quite colorless, chromium may be considered absent. Filter the mixture, washing with water, and dry and ignite the insoluble residue on the filter. Now grind it with ten times its weight of sodium carbonate and a little potassium nitrate, fuse the mixture and extract with water, etc., as before. Filter and add the filtrate to the former one. Acidify the combined filtrates with hydrochloric acid and evaporate to dryness to render the silica insoluble and reduce the chromic acid to Cr_2O_3. Take up in hydrochloric acid, dilute, and filter. Precipitate the Cr_2O_3 and Al_2O_3 in the filtrate with ammonia. Boil for a short time, filter, and wash well with hot water. Dry and ignite the precipitate and then fuse it with as little sodium carbonate and potassium nitrate as possible. Extract the melt with water and transfer the mixture to a platinum dish. Evaporate the liquid until it is very concentrated, adding crystals of ammonium nitrate from time to time to change all the carbonated and caustic alkali to nitrate. Each addition of the ammonium nitrate produces an effervescence and ammonium carbonate is given off. The solution finally becomes almost syrupy and smells faintly of

* Mainly from Blair. Chemical Anal. of Iron.

ammonia, the addition of ammonium nitrate no longer causing an effervescence. Now add a few drops of ammonia and filter from the precipitated alumina, aluminum phosphate, manganese dioxide, etc. The filtrate contains the chromium as alkali chromate. Add an excess of a strong solution of sulphur dioxide, which changes the color of the solution from yellow to green. Boil well, add an excess of ammonia, boil again for a few minutes, filter on an ashless filter, and wash thoroughly with hot water. Dry and ignite the precipitate and weigh as Cr_2O_3. Multiply the weight by 0.6842 to obtain that of the chromium.*

2. **Method for Chrome Iron Ore.**—Grind the ore in an agate mortar to the finest possible powder. Weigh 0.5 gram into a spun-iron crucible of about 20–25 cc. capacity. Add about 5 grams of sodium peroxide and mix thoroughly with a glass rod. Good sodium peroxide is of a yellowish color. Reject any that is white, as it has become decomposed. Holding the crucible with tongs, heat over a Bunsen burner. The operation requires careful watching. Only a low red heat is necessary, but as the mass is slow in fusing, one is apt to heat the bottom of the crucible to bright redness. When this happens the peroxide is likely to attack the crucible and perforate it. If care is taken, and the crucible is tipped from side to side, the mass gradually softens and becomes liquid around the sides. Now give the crucible a rotary motion, never allowing the temperature to become much higher than a low red heat, until all unfused material, floating in the center, has liquefied like the rest. When the rotary and tipping movements have been continued for several minutes more, the operation may be considered finished. If manipulated as described, the same crucible should serve for many fusions; otherwise the crucible and analysis may easily be ruined.

3. Have ready a 4-inch porcelain casserole containing about $\frac{3}{4}$ in. of cold water, or somewhat less than the height of the crucible. Set the partially cooled crucible carefully in this, avoiding the entrance of any water. Cover the casserole, and, as soon as apparently safe, insert a glass rod under the cover and upset the crucible. The contents will quickly boil out and disintegrate without any further heating. When the action is over, remove and rinse the cover, lift out the crucible on the rod and wash the outside with cold water. Now, holding the crucible with the fingers, similarly rinse out the inside. Again

* $152 : 104 = 1 : x$. $x = 0.6842$.

replacing the cover, heat the mixture to boiling and then boil gently for ten minutes by the watch. This is to make certain that all the peroxide present is decomposed. If the volume of liquid gets low, add hot water. Remove from the heat, dilute somewhat with cold water, and then lift the edge of the cover and quickly add about 5 grams of ammonium carbonate. The dilution and cooling are to lessen any possible effervescence. The ammonium carbonate neutralizes a portion of the sodium hydroxide and renders the solution less likely to destroy a filter. It must not be added, however, until the sodium peroxide has been decomposed by boiling, as otherwise some ammonium nitrite would be formed that would subsequently cause a high result. As soon as the ammonium carbonate has dissolved, the mixture is ready for filtration.

4. Filter, washing several times with hot water. The filtration is best done with the use of a Witt's plate and suction, in which case four washings are usually sufficient.

The filtrate now contains the chromium as sodium chromate. Transfer it to a flask of about a liter capacity and cool under the tap. Have ready some cold 1 : 1 hydrochloric acid. Pour this into the chromium solution very cautiously (on account of effervescence) until the latter is plainly acid. This is usually shown by the change of color from yellow to orange.* If the color change is not apparent, litmus paper may be used, but not left in the solution. Now add about 25 cc. more of the same 1 : 1 acid, dilute if necessary to 300–400 cc., and see that the solution is perfectly cold. It is now ready for the titration.

5. If potassium iodide be now added, the chromic acid present will liberate iodine,[1] which is then titrated with a standard solution of sodium thiosulphate.[2] Allow about 1 gram of potassium iodide for every 20 per cent of chromium possibly present. Never use less than 1 gram. More may be added at the end of a titration, as a test, and the titration continued on any additional iodine set free, without vitiating the final result. It is convenient to employ a 50 per cent solution of potassium iodide with a short 2-cc. pipette in the bottle. After adding the potassium iodide, titrate at once with the standard thiosulphate until the brown color of the iodine has become faint.

* Neutral chromate is changed to dichromate:

$$2(K_2O.\ CrO_3)+2HCl \rightarrow K_2O\cdot Cr_2O_6+2KCl+H_2O.$$

Now add a few cubic centimeters of starch solution (COPPER, 3) and continue the titration cautiously, until a single drop completely discharges the last trace of color produced by the starch and leaves the solution a clear, pale green or bluish-green tint if there be much chromium present. The end-point is very sharp, and without care is very easily passed. Multiply the number of cubic centimeters of thiosulphate used, by the percentage value for chromium of 1 cc. to obtain the result.

If the end-point be passed, add potassium permanganate of any strength, drop by drop, from a burette, counting the drops, until the blue color is restored.[3] Again finish the titration and note the burette reading; then add the same number of drops of permanganate as before, and once more finish with the thiosulphate and note reading. Deduct this additional amount of thiosulphate from the previous reading to obtain the true reading for chromium.

6. The thiosulphate solution used for copper may be employed (see COPPER), in which case the copper value multiplied by 0.2727 will give the chromium value. This solution is inconveniently weak when there is much chromium present, requiring over 3 cc. for 1 per cent. With a solution containing about 36 grams of thiosulphate per liter, 1 cc. will equal about 0.5 per cent of chromium, on the basis of starting with 0.5 gram of ore. To preserve the solution add about 4 grams of sodium hydroxide per liter (see COPPER, 1). Standardize with permanganate, as described in COPPER, **4**, using at least 40 cc. of the permanganate. The previously determined Fe value of 1 cc. of the permanganate multiplied by 0.3105 will give the Cr value. That is, if 1 cc. = 1 per cent of iron, it will be equivalent to 0.3105 per cent of chromium, or, 1 cc. will liberate as much iodine as 0.3105 per cent of chromium. Titrate the iodine liberated, which is equivalent to the determined amount of chromium, with the thiosulphate, to obtain the value of 1 cc. of the thiosulphate in chromium.

The thiosulphate solution may also be standardized against potassium dichromate; 0.283 grams of pure potassium dichromate are equivalent to exactly 20 per cent of chromium, on the basis of 0.5 gram of ore taken for assay. Weigh this amount of the dry powdered salt and transfer to a flask of about a liter capacity, add about 400 cc. of cold water and about 30 cc. of 1 : 1 hydrochloric acid. Cool under the tap, add 2 grams of potassium iodide and titrate with the thiosulphate. Divide the 20 per cent of chromium present by the number

of cubic centimeters of thiosulphate used, to find the percentage value of 1 cc.

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[1] The reaction between chromic acid and potassium iodide is, $CrO_3+6HCl+3KI \rightarrow CrCl_3+3KCl+3H_2O+I_3$. According to the reaction, 1 Cr requires 3KI, or, 52 parts by weight of Cr require 498.06 parts of KI. One per cent of Cr, or 0.005 gram, would then require 0.04789 gram of KI. Twenty per cent would require 0.9578 gram of KI, or, roughly, 1 gram.

[2] The reaction between sodium thiosulphate and iodine is, $2(Na_2S_2O_3)+2I \rightarrow 2NaI+Na_2S_4O_6$. Sodium iodide and tetrathionate are formed.

[3] Potassium permanganate, like chromic acid, is an oxidizing agent and liberates iodine from potassium iodide in the same way. Leaving out the concurrent reactions, which are all included in the complete reaction shown in Note 1, above, the oxidation of the KI may be shown as follows: $2KI+O=K_2O+I_2$. Of course this reaction does not take place by itself, but only in the proper chemical environment.

[4] In the case of copper (see COPPER, 2), Cu = I. The above reaction in Note 1 shows that $Cr=I_3$; accordingly, 3Cu = Cr, or, from the atomic weights, 190.71 Cu = 52 Cr. This gives 1 Cu = 0.2727 Cr.

[5] The reaction in Note 3 shows that $O=I_2$. The reaction in Note 1 shows that $Cr=I_3$. Then $O_3=I_6$ and $Cr_2=I_6$, making $Cr_2=O_3$. Now when a ferrous salt is oxidized, the FeO is changed to Fe_2O_3, that is, $2FeO$, or $Fe_2O_2, +O=Fe_2O_3$. This makes $Fe_2=O$ and $Fe_6=O_3$. Comparing this with the Cr ratio for O, we have $Fe_6=Cr_2$, or, $Fe_3=Cr$. By weight, then, 167.52 Fe = 52 Cr, or 1 Fe = 0.3105 Cr.

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7. Another Method for Chrome Iron Ore.—While I personally prefer the method just described, I formerly employed the following, adapted from Blair.*

Proceed exactly as in 2, 3 and 4 of the previous method, and then continue as follows:

8. Acidify the filtrate with dilute sulphuric acid (1 : 4) and then add a considerable excess—25 cc. or more. After allowing the solution to cool, transfer it to a battery-jar (such as that used for iron titrations (IRON, 7) and dilute to 700 cc. with cold water.

9. The chromium in the solution now exists as chromic acid. It is determined by reduction with ferrous ammonium sulphate. A weighed amount of the powdered salt, in excess of what is actually required, is added, and the exact excess is determined by titrating it with standard permanganate, the balance being what was consumed by the chromic acid. A basis for calculating the chromium is thus obtained. The regular permanganate used for iron may be employed. It should

* Chemical Anal. of Iron.

have been carefully standardized against Sorensen's salt or oxalic acid (see IRON, 11) and then calculated to iron.

10. The reduction and titration of the chromium solution are carried out as follows:

Place several grams of the powdered and well-mixed ferrous salt in a weighing-bottle and carefully weigh the whole; then add the salt gradually, in small portions, to the chromium solution, while stirring, until the yellowish color has apparently entirely disappeared. Now, with the burette filled to the zero mark, run in a little of the permanganate. If it is decolorized on stirring, the iron salt is in excess, otherwise more iron salt should be added until a plain excess is attained. The permanganate used in testing counts as part of the whole used in the titration. Determine the amount of the excess of iron salt by running in more permanganate until the first perceptible permanent change of tint is observed. This gives a more accurate end-point than titrating to a noticeable pink tint, since the green color of the reduced chromium tends to neutralize a faint pink. Now re-weigh the bottle of ferrous salt and note the total amount used. The next step is to determine the value of 1 cc. of the permanganate in the ferrous salt used, as the latter is seldom pure. Add about 1.5 grams more of the ferrous salt to the titrated solution, again re-weighing the bottle to determine the exact amount taken. Refill the burette and again titrate to the same end-point as before. This will show the value of 1 cc. in this particular ferrous salt. Apply this value of the permanganate to the previous titration in determining the excess of ferrous salt.

11. The amount of ferrous salt consumed by the chromium has been arrived at by deducting the excess found from the total quantity taken in the chromium titration; it is now necessary to know the percentage of purity of the ferrous salt. This may be calculated from the last titration. The permanganate, as standardized for iron, will show, from the cubic centimeters required for the weight of iron salt taken, the true percentage of ferrous iron in the iron salt. It should be 14.24 per cent if the salt is pure. The figure found is usually lower and its percentage of 14.24 should be calculated. This may be considered as the percentage of purity of the salt. Apply this correction to the weight of iron salt consumed by the chromium before calculating the latter.

12. To reduce 52 parts of chromium in chromic acid to Cr_2O_3, 167.52

parts of ferrous iron are required; or 1 part Fe = 0.3105 parts Cr.* Ferrous ammonium sulphate ($FeSO_4(NH_4)_2SO_4+6H_2O$) contains 14.24 per cent of ferrous iron; therefore 1 part of the salt = 0.04421 parts of chromium. Accordingly, multiply the corrected weight of the salt consumed by the chromium by 0.04421 to obtain the weight of the chromium sought, or by 0.06462 to obtain that of the Cr_2O_3.

13. Method for Steel.†—This method is based upon the well-known fact that chromic salts can be oxidized completely to chromic acid by the addition of potassium chlorate to a concentrated nitric acid solution, and also upon the fact that the presence of nitric acid does not interfere with the titration of chromic acid in a cold solution by means of ferrous sulphate and permanganate.

Weigh 3 grams of steel into a 400-cc. flask, add 35 cc. of strong hydrochloric acid, and boil for five or ten minutes, which will be found sufficient to dissolve completely even the highest chrome-steels. When most of the hydrochloric acid is boiled off, add 150 cc. of strong nitric acid and continue the boiling until no more brown fumes are seen at the mouth of the flask, showing that the hydrochloric acid has all been driven off. Remove the flask from the flame or hot plate, allow to cool for two or three minutes, and then add 10 grams of potassium chlorate in crystals. It is best to allow the solution to cool somewhat before adding the chlorate, in order to diminish the violence of the effervescence due to the action of the chlorate on the chromic salts. Replace on the hot plate and boil down to about 40 cc. in order to completely decompose the potassium chlorate. It is necessary to decompose the chlorate completely, or results will be from 0.1 to 0.2 per cent high, but the amount of nitric acid left in the solution is unimportant. At this stage the chromium will all be in the solution in the form of chromic acid. Any manganese will be precipitated as dioxide, and generally some crystals of potassium nitrate arising from the decomposition of the chlorate will have separated out. Add 100 cc. of water and a few drops of hydrochloric acid. This will at once dissolve the manganese dioxide without action on the chromic acid. Boil the solution for a few minutes to remove the chlorine set free by the reduction of the manganese dioxide, and then cool to room temperature. Make the cold solution, contained in a battery-jar, up to

* See Note 5 to preceding method.

† From paper read by A. G. McKenna before the Chemical Section of the Engineers' Society of Western Pennsylvania, June 18, 1896.

700 cc. with cold water, and add a weighed excess of ferrous ammonium sulphate, as described in **10**, above. Finally, titrate the excess of ferrous salt with permanganate and calculate the result as in **11**, **12**.

In very many chrome-steels the amount of manganese is so inappreciable in comparison with the chromium that for practical results it is not necessary to dissolve the dioxide as described above, but the solution after the evaporation to 40 cc. may be diluted and titrated at once.

14. Rapid Method for the Determination of Chromium in Chrome and Chrome-nickel Steel.*—Dissolve 1 gram of the steel by warming in a large covered beaker with 25 cc. of the acid mixture described below. When solution is complete, remove from the heat and add about 15 or 20 cc. of cold water. Rotate the liquid in the beaker and drop in at once about 1 gram of sodium bismuthate and continue to rotate the mixture for a few seconds. Now heat to boiling and boil rapidly. The permanganate formed by the sodium bismuthate will be rapidly decomposed and there will remain a clear violet liquid (manganic metaphosphate). Further boiling will complete the conversion of the chromium to CrO_3.

Decompose the excess of manganic metaphosphate with $\frac{1}{2}$ cc., or more if necessary, of dilute hydrochloric acid and boil one minute. Cool somewhat, dilute to 200 cc. with cold water, add a slight excess of ferrous ammonium sulphate (as in **10**) and titrate with permanganate. Calculate the result as in **11**, **12**.

The end-reaction is very sharp, the results are accurate and an analysis can be completed in ten minutes. The method has not yet been tested in presence of tungsten and molybdenum.

Acid mixture for dissolving the steel:

300 cc. nitric acid, 1.42 sp. gr.
300 cc. sulphuric acid, 1 part acid, 3 parts water.
300 cc. water.
100 cc. phosphoric acid, 85 per cent.
$1\frac{1}{2}$ grams manganese sulphate.

* N. M. Randall, Mining Science, LXI, 56.

CHAPTER XIII

COPPER

During the many years that the iodide method for copper has been used in my laboratory it has been constantly studied, and from time to time slightly modified, until it is now the most accurate practical method for ores with which I am acquainted.

While the accuracy of the electrolytic method cannot perhaps be exceeded, the electrolytic method as actually carried out in some laboratories is liable to give erroneous results, principally owing to the failure to remove interfering impurities found in many ores. The proper removal of these impurities is apt to be quite tedious and to involve considerable manipulation, tending to cause loss. I therefore give the iodide method the preference in most cases, as being more practical and nearly if not quite as accurate as the electrolytic at its best.

1. **Iodide Method.***—A standard solution of sodium thiosulphate is required. Make up a solution containing about 19.5 grams of the pure crystals to the liter.[1] To prevent decomposition by CO_2, also add about 4 grams of sodium or potassium hydroxide per liter. This will not interfere with either the copper or the lead titration. The solution is best kept in an amber glass bottle. Under these conditions it is very stable.

The thiosulphate solution may be standardized as follows:

2. Weigh carefully about 0.2 gram of pure copper-foil and place in an 8-oz. flask (Whitall Tatum Co., pear-shaped) †. Add, best from a small pipette, 5 cc. of strong nitric acid (sp. gr. 1.42) which will quickly dissolve the copper. Dilute the solution a little and boil to expel the red fumes. Now dilute to about 40 cc. and add ammonia in slight excess. Again boil until the ammonia odor is faint and then add a marked excess of glacial acetic acid and continue the boiling for about a

* Author's modification.

† I usually refer to this as a "copper flask."

minute longer. This last boiling is important, as it effects the neutralization or expulsion of any remaining oxidizing compounds that would cause a return of the blue color after titration. See that no copper salt remains undissolved. Cool to room temperature and add 6 cc. of a 50 per cent solution of potassium iodide, or 3 grams of the solid. Cuprous iodide will be precipitated and iodine liberated according to the reaction,

$$2(Cu.2C_2H_3O_2)+4KI \rightarrow Cu_2I_2+4(K.C_2H_3O_2)+2I.$$

The free iodine colors the mixture brown. Titrate at once with the thiosulphate solution until the brown tinge has become faint and then add sufficient starch solution to produce a marked blue coloration. Continue the titration cautiously until the last faint lilac tint is entirely removed by a single drop. In the case of an ore, the presence of lead or bismuth may change the color of the final tint, but the end-point is equally sharp, especially if the last few drops of thiosulphate are allowed to fall into the center of the slowly rotating liquid, and any change from the surrounding surface noted. One cubic centimeter of the thiosulphate solution will be found to correspond to about 0.005 gram of copper, or about 1 per cent in the case of an ore where 0.5 gram has been taken for assay. The reaction between the thiosulphate and the iodine is

$$2(Na_2S_2O_3)+2I \rightarrow 2NaI+Na_2S_4O_6.$$

Sodium iodide and tetrathionate are formed.

3. Improved Determination of End-point.—With low-grade coppers the end-point is very sharp, but with high-grade material the large amount of precipitated cuprous iodide usually possesses a faint purplish tinge that is indistinguishable from the last traces of color due to the starch iodide. The addition of a little dilute silver nitrate solution (say 1 cc. of a solution of 100 mg. of silver nitrate in 100 cc. of water) will cause the precipitation of a small amount of silver iodide, the slight yellowish color of which will neutralize the purplish tinge of the cuprous iodide, and thus render the end-point of the starch solution appreciably sharper.

4. Usual Method of Standardizing the Thiosulphate.—In the method of standardizing previously described, pure copper-foil is used. This is usually difficult to obtain, necessitating a determination of the actual copper value of the foil used. This trouble is avoided by the equally accurate and much shorter method of standardization

as follows: Place about 100 cc. of cold water in an 8-oz. flask. Add about 5 cc. of glacial acetic acid, and then run in from a burette about 35 cc. of the ordinary permanganate solution used for iron (IRON, 2). Now add 6 cc. of 50 per cent potassium iodide* solution and titrate with the thiosulphate solution while the permanganate burette is draining. When near the end, add a little starch solution and finish the titration carefully. The end-point is very sharp, no silver nitrate being necessary. If the end-point is accidentally passed, add a little more permanganate and repeat. Finally, read both burettes. Multiply the Fe percentage value of 1 cc. of the permanganate by 1.139 to obtain the copper value.[2] Multiply this by the number of cubic centimeters of permanganate used, and divide the result by the number of cubic centimeters of thiosulphate required. This gives the percentage value of 1 cubic centimeter of the thiosulphate in copper. All the figures are based on the assumption that 0.5 gram of material has been taken for determination.

5. Starch Solution.—The following solution is the result of personal experiment: Make a cold saturated solution of commercial sodium chloride in distilled water and filter it. To 500 cc. of this solution add 100 cc. of glacial acetic acid and 3 grams of starch. Mix cold. Boil until nearly clear, about two minutes. Add a little water to replace that lost by boiling, perhaps 25 cc. A true solution of all the starch is thus obtained. No filtering or settling is required and the solution may be cooled and used at once. It keeps indefinitely and gives sharper end-points than the ordinary starch liquor.

6. Treatment of an Ore.—To 0.5 gram of the ore in an 8-oz. flask add 10 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid. Boil until decomposition is complete, using more of the acids if necessary (and enough at the end to hold all soluble salts in solution), and then add 8 cc. of strong sulphuric acid and boil to abundant fumes, best over a free flame, but do not boil off much of the sulphuric acid.†

After cooling, boil with about 30 cc. of water for a moment and then allow to stand, hot, until any anhydrous ferric sulphate has entirely dissolved; then filter through a 9-cm. filter to remove more especially any lead sulphate. Receive the filtrate in a beaker about 6-cm. in diameter. Wash the filter and residue at least six times with hot water.

* 50 grams of KI dissolved in water and diluted to 100 cc.

† If impure sulphur separates, it is best cleaned by allowing the strong sulphuric acid to continue just at a boil (so as not to evaporate much) for some time.

The final volume of the filtrate will ordinarily not much exceed 75 cc. Place in the beaker a piece of stout sheet aluminum about an inch and a half square and with the alternate corners bent in opposite directions for about a quarter of an inch, so as to prevent the plate from lying flat on the bottom. (The same aluminum may be used repeatedly as it is but little attacked each time.)

7. Cover the beaker and heat to boiling. After boiling about ten minutes the copper should be all precipitated, if the volume of the solution did not much exceed 75 cc. As a test, inject a little hydrogen sulphide water from a wash-bottle through the lip of the beaker. If more than a faint brown color is produced, boil longer, until the solution clears by coagulation of the precipitate, and again test. Do not boil to very small bulk, as some of the precipitated copper might then redissolve. Add water, if necessary, to prevent this. The hydrogen sulphide test will finally become negative, or show only a faint brownish tinge. Now remove from the heat and wash down the cover and sides of the beaker with hydrogen sulphide water. This will prevent any of the finely divided copper from becoming oxidized and dissolved and will also precipitate any traces of copper that may still remain in solution. (It should be understood that there is no difficulty in precipitating *all* the copper as metal in every case.)

Decant through a 9-cm. filter (using a loop funnel by preference), and then, without delay, rinse the copper into the filter with a jet of hydrogen sulphide water, leaving the aluminum, as clean as possible, in the beaker. Traces of adhering copper will be recovered later. Wash filter and precipitate six times with hydrogen sulphide water. Allow to drain completely each time; but never permit the filter to remain drained a single moment, until the washing is finished, or copper may oxidize and run through.

8. Now place the original clean flask under the funnel, then open the filter carefully and spread it smoothly in the funnel, against one side. With a jet of hot water, using as little as possible, wash the precipitate into the flask. If it is apparently too bulky to pass easily through the funnel, proceed as follows: Support the paper, scoop-shaped, in the hand, over the flask, and wash in the main portion of the precipitate, then replace it in the funnel, with the flask underneath, and wash in the remainder.

Pour 5 cc. of strong nitric acid over the aluminum in the beaker, shake it about so as to dissolve any adhering copper, and then pour

from the beaker over the filter, still retaining the aluminum in the beaker. Without washing beaker or filter at this stage, collect the filter into a small compass with a glass rod, and push it gently, with moderate compactness, into the apex of the funnel. Level the top of the mass, but avoid compressing so tightly as to greatly impede filtration. Next, remove the flask and replace it with the beaker.

Boil the mixture in the flask to dissolve the copper and expel the red fumes. If the liquid is too dilute, so that the copper fails to dissolve immediately, continue boiling until solution of everything is complete, including any copper sulphide present. Finally, again place the flask under the funnel. Now pour over the filter 5 cc. or more of saturated bromine water, or enough to impart a distinct color to the liquid in the flask. The bromine cleanses any residue still adhering to the filter, but its most important function is to insure the highest state of oxidation of any arsenic or antimony in the solution.[3] Now wash the beaker and aluminum with hot water, pouring through the filter, then wash the filter six times. The final volume in the flask need not much exceed 50–60 cc.

Boil the solution until the excess of bromine is entirely expelled and the volume is reduced to perhaps 25 cc. Cautiously add a small excess of ammonia, to the boiling liquid, allowing it to run slowly down the side of the flask (usually 10 cc. or a little more). Boil off most of the excess, that is, until the odor is faint. Now add 5 cc. of glacial acetic acid and boil for about a minute more. This last boiling is very important, as it tends to remove the last traces of oxidizing compounds that might cause a return of the blue color at the end of the titration. Cool completely under the tap.

Dilute to about 30 cc., if necessary, add potassium iodide in the porportion of 2 cc. of a 50 per cent solution for every 15 per cent of copper assumed to be present, but never less than 2 cc. in any case, and titrate with standard sodium thiosulphate solution as described for the standardization. Multiply the cubic centimeters of thiosulphate required by the percentage value of 1 cc. to obtain the result.

9. It is best to boil off as much of the free ammonia as possible, before acidifying with acetic acid, in order to avoid the formation of too much ammonium acetate, which has a retarding effect on the reactions of the subsequent titration. The point cannot be told, if much copper is present, by the absence of an ammoniacal odor, as the blue copper-ammonium salt gradually decomposes and gives off

ammonia. It is usually best to add the acid when the smell of ammonia has become rather faint. Boiling too long does no harm unless a bluish deposit forms on the flask. This may be copper arsenate or hydroxide, which frequently dissolves with great difficulty in acetic acid. Always look for this deposit before adding the acetic acid, and, when observed, cautiously add enough ammonia to dissolve it, again boiling off any great excess. A precipitate of any nature, due to overboiling, which does not deposit on the flask, will usually do no harm, and the copper contents will be subsequently taken up by the acid. A light-colored flocculent precipitate, sometimes observed in the acetic acid solution, perhaps aluminum hydroxide, is ordinarily without effect. If the cooling, before titration, causes the separation of crystals of copper acetate, they should be redissolved by warming with a little more water and the solution again cooled.

10. **Notes.**—According to the equation previously given, 0.5 gram of copper requires 2.61 grams of potassium iodide. While direct experiment shows this to be apparently true, yet when only the theoretical amount of potassium iodide is present the reaction is slow, and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is always best, therefore, to use an excess, but as the iodide is expensive the quantity used should be governed by the amount of copper present, which can always be estimated approximately. Allow, say, 1 gram of potassium iodide for every 15 per cent copper, when 0.5 gram of ore is taken for assay. It is convenient to prepare a solution containing 50 grams of potassium iodide in 100 cc. A 2-cc. pipette will thus deliver 1 gram of the salt. No error will be introduced in a doubtful case by adding more potassium iodide after the titration is apparently finished and resuming the operation if the blue color is thereby restored.

11. Zinc and silver do not interfere with the assay. Lead and bismuth are without effect, except that by forming colored iodides they may mask the approach of the end-point before adding starch. Arsenic and antimony, under the treatment described, have no influence. The return of the blue tinge in the titrated liquid after long standing is of no significance, but a quick return, which an additional drop or two of the thiosulphate does not permanently destroy, is usually an evidence of faulty work.

12. In such a case it is not necessary to begin the determination anew. The following procedure will permit a repetition of the titra-

tion: Add 10 cc. of strong nitric acid and heat the mixture to boiling. Heat very cautiously at first until the iodine set free is mostly expelled; otherwise the mixture may foam over. Now manipulate the flask in a holder over a free flame and boil the solution down as rapidly as desired until only about 5 cc. are left. Dilute with 25 cc. of hot water and boil again for a short time to expel any red fumes. Now add a slight excess of ammonia and finish in the usual manner.[4]

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[1] At the rate of 19.53 grams per liter, 1 cc. of the solution will theoretically equal 0.005 gram of copper, or 1 per cent on the basis of 0.5 gram of ore being taken for analysis. The figure may be arrived at by considering the reactions given in 2. The first reaction shows that $2Cu = 2I$, or, $Cu = I$. The second reaction shows that $2(Na_2S_2O_3) = 2I$, or, $Na_2S_2O_3 = I$. This makes $Cu = Na_2S_2O_3$, or, considering atomic weights, 63.57 parts by weight of $Cu = 158.12$ parts of $Na_2S_2O_3$. The formula of crystallized thiosulphate, however, is $Na_2S_2O_3 + 5H_2O$. The molecular weight of the crystallized salt, then, is 248.20 instead of 158.12. We can now make the proportion $63.57 : 248.2 = 0.005 : x$. $x = 0.01953$. This is the weight, in grams, of pure crystallized thiosulphate which is equal to 0.005 gram, or 1 per cent of copper. This amount should be in 1 cc., equal to 19.53 grams per liter. There need be no special effort to make a theoretically correct solution. The purity of the thiosulphate cannot be depended on, and, in any event, the crystals may have lost some of their combined water by drying. An approximately correct solution, occasionally re-standardized, is quite sufficient.

[2] Both cupric copper and permanganate are oxidizing agents which act on potassium iodide and liberate iodine. The simplified reaction may be considered as follows: $2KI + O = K_2O + 2I$. 1 oxygen thus liberates 2I. Note 1, above, shows that $2Cu = 2I$; therefore $2Cu = O$. Now when ferrous iron is oxidized, the change is from FeO to Fe_2O_3. Thus $2FeO$, or, $Fe_2O_2, + O = Fe_2O_3$. This shows that $2Fe = O$, which, compared with the above Cu ratio, gives $2Fe = 2Cu$, or, $Fe = Cu$. Introducing the atomic weights, we have 55.84 Fe = 63.57 Cu, or, 1 Fe = 1.139 Cu.

[3] The reaction, in case any *ous* compounds of arsenic or antimony are present, is in accordance with the following: $H_3AsO_3 + Br_2 + H_2O \rightleftarrows H_3AsO_4 + 2BrI$. This reaction is reversible, but, under the conditions prevailing, proceeds as shown. It is easily realized that if bromine is not thus allowed to convert the *ous* to *ic* compounds, the liberated iodine will do it later, and any iodine thus consumed will cause a correspondingly low copper result.

[4] A simple method of determining the true end-point, when it has been slightly passed, is as follows: Add, from a burette, a counted number of drops of permanganate, of any strength, until the color returns. Continue the titration carefully to the end and take reading of burette. Now add the same number of drops of permanganate as before, and again titrate and take reading. Subtract the amount of thiosulphate last required from the previous reading to obtain the true reading. *Example*: Had passed the end-point at 16.8 cc. After adding 5 drops of permanganate the blue color was restored. Reading, 17.2 cc. Added 5 drops more

and again titrated. Reading, 18.1 cc. Difference from last reading, 0.9 cc. Subtract this from last reading, 17.2 − 0.9 = 16.3, the true end-point.

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13. Short Iodide Method.*†—To 0.5 gram of the ore in an 8-oz. "copper flask" add 10 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid. Heat gently to decompose the ore, then add 4 cc. of strong sulphuric acid and boil almost to dryness, best over a free flame with the flask in a holder. Allow to cool.

Add 50 cc. of water and heat to boiling, then add 5 cc. of strong bromine water and boil until all the bromine is expelled. By this time all anhydrous ferric sulphate should be in solution.

Remove from the heat and cautiously add strong ammonia until its effects are plainly apparent, by a partial precipitation of ferric hydroxide or otherwise, but avoid an unnecessary excess.

Now add 7 cc. of glacial acetic acid, or sufficient to render the solution strongly acid. Boil for about half a minute and then cool completely under the tap.

Add 2 grams (usually roughly measured after trial) of powdered sodium fluoride, and then, after mixing, 4 cc., more or less, of potassium iodide solution containing 50 grams in 100 cc.

Titrate with standard sodium thiosulphate solution (about 19.5 grams per liter) until the brown iodine color is faint, then add a little starch liquor and continue the titration until the last drop, falling into the center of the nearly quiescent liquid in the flask, produces no further decolorization. It is best to read the burette just previous to this last drop trial, as the addition may prove to be unnecessary.

It is usually safer to now add a little more potassium iodide, to see if the operation is actually finished, and continue the titration if the additional iodide causes a return of the blue tinge.

The following elements do not interfere: As, Sb, Sn, Hg, Zn, Cd, U, Ni, Co, Fe, Mn, Bi, Mo, Ag, Pb. Vanadium interferes. Chromium interferes by forming an insoluble anhydrous sulphate which holds copper. It similarly interferes in the long method. The trouble may be avoided by using no sulphuric acid in the decomposition.

A noticeable feature of this short method is the larger excess of

* Maier, Eng. and Min. Jour, Feb., 1819, pp. 372–3. Modified by the author.

† According to my personal tests the results obtained by this method are apparently as accurate as those by the long method. In almost every instance I unhesitatingly give this method the preference. About the only objection I have found is the greater amount of potassium iodide usually required, this being an expensive salt.

potassium iodide required. This is apparently due to the larger excess of salts in solution than in the long method, these salts retarding the reactions, although certain elements appear to show this effect more than others, especially Ni, Co, Mo and U.

14. **Electrolytic Method.**—To 1 gram of the ore in an 8-oz. flask add 10 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid. Boil gently until decomposition is complete, using more of the acids if necessary. If the evaporation of the liquid causes a separation of soluble salts, add enough hydrochloric acid at the end to again bring them into solution. Finally, add 8 cc. of strong sulphuric acid and boil, best over a free flame, to abundant fumes. After cooling, boil with about 30 cc. of water for a moment and then allow to stand, hot, until any anhydrous ferric sulphate has entirely dissolved. If silver is likely to be present add a single large drop of strong hydrochloric acid just previous to the boiling, to precipitate it as chloride. Filter, washing filter and residue at least six times with hot water. Dilute the filtrate to about 300 cc. (the dilution is unnecessary if the amount of copper is small) and pass in hydrogen sulphide until the copper is all precipitated, as shown by the clear condition of the supernatant liquid. Filter off the sulphides, washing well with hydrogen sulphide water. Now rinse the precipitate back into the beaker as completely as possible, with hot water, place the beaker under the funnel and pour through the latter a hot mixture of 5 cc. of a moderately strong colorless solution of sodium sulphide and 15 cc. of water. Remove the beaker, stir the contents well, and, either immediately or after warming a few minutes, according to the amount of arsenic and antimony apparently present, filter through the last filter again. A second extraction is rarely necessary. Wash out the beaker with hot water and then wash the precipitate well with hot dilute sodium sulphide solution. Reserve the filtrate, which almost invariably contains a little dissolved copper. Rinse the residue back into the beaker with hot water, using as little as possible. It is difficult to get the filter very clean and it is not necessary. Place beaker and contents once more under the funnel and pour through the latter a hot solution of about 2 grams of potassium cyanide in about 15 cc. of water. Remove the beaker and replace it with the original flask. Heat and stir the mixture in the beaker until the copper sulphide is all dissolved, adding more potassium cyanide if required, but avoiding a great excess. Sulphides of bismuth, cadmium, etc., will remain undissolved. Again filter through the last filter and wash ten times

with hot water. Use small washes each time to avoid a bulky filtrate. Remove flask and filtrate to a hood, add 5–6 cc. of strong sulphuric acid (this is usually a sufficient excess), heat to boiling and boil to fumes. Finally, finish over a free flame until nearly all the excess of acid is expelled. Allow to cool with the flask inclined, to prevent the cake which may form from cracking the glass. The addition of a little nitric acid to the sulphuric acid mixture causes a more rapid solution of the copper sulphide, but this is a disadvantage, as the mixture is then liable to bump badly. Dissolve the cool cake or residue in about 25 cc. of water. During these operations attention may be turned to the reserved filtrate, which usually contains an appreciable amount of copper. Acidify it with hydrochloric acid, stir well to coagulate the precipitated sulphur, filter, and wash with hydrogen sulphide water. Ignite the filter and contents in a platinum dish at a dull-red heat until the carbon of the paper is entirely consumed. Be very careful to do this at as low a temperature as possible. All the arsenic and antimony will be expelled. Warm the residue with a few drops of nitric acid and add the solution to the main portion in the flask. To the latter now add 3 cc. of strong nitric acid, transfer the solution to a suitable beaker, dilute, and electrolyze as described below.

15. Electrolysis of the Copper Solution.—The solution should have a volume of about 125 cc. and contain several cubic centimeters of strong nitric acid (sp. gr. 1.42). The amount of free nitric acid necessary is not narrowly limited. It is gradually changed to ammonia by the electrolysis, and therefore, if too little be present, the solution may become alkaline. On the other hand, too much acid retards or may prevent the deposition of the copper. I usually use an excess of about 3 cc. in the above volume of liquid, but 7 or 8 cc. may be safely employed, with the advantage of preventing, in a large measure, the deposition of any arsenic that may have escaped extraction.

The following apparatus may be used: A cathode consisting of a plain platinum cylinder 5 cm. long and 2.5 cm. in diameter. It has a total surface of about 78.5 sq. cm. and weighs about 12.5 grams. It is supported by a strong platinum wire attached to the top. An anode consisting of a stout platinum wire rising from the center of a base made by coiling the wire around itself closely so as to form a circular disk. It weighs about 8.5 grams. A beaker suitable for the above electrodes, having a diameter of about 5 cm. and a height of about 8–9 cm.

The volume and acidity of the solution having been properly

adjusted and the cathode cleaned, ignited, and weighed, the electrodes are inserted and suitably supported in the beaker, and the latter is covered with a split watch-glass, which permits the wires to pass through the center, leaving an opening of only a small crack. Adjust the anode within the cathode with its base almost touching the bottom of the beaker. The bottom of the cathode should come about one-fourth of an inch above the base of the anode, and the top of the cylinder should project a little above the surface of the solution.

Now connect with the battery and electrolyze. The cathode should be connected with the zinc pole of the battery. The current density should be ND_{100} = 0.5–1 amp. Electrode tension, 2.2–2.5 volts. Temperature, 20°–30° C. Time required, four to five hours. For details as to the attainment of these conditions see ELECTROLYSIS, 7. (In my own work, using a direct 220-volt current from a dynamo and a bank of lamps as a resistance—which reduces the tension to about 2.2 volts—I usually employ, with the above apparatus, from 0.2 to 0.4 amp., according to the amount of copper present, and allow to run overnight.)

When the solution has become colorless and the copper is apparently all deposited, immerse the cathode deeper in the liquid, or better, raise the level of the latter by rinsing the cover and sides of the beaker, and allow the current to run for half an hour longer. The fresh platinum surface will show whether copper still remains in solution. Finally, at the end, lower the beaker from the electrodes, with the current still passing, and at the same time rinse off the adhering acid solution with a stream from the wash-bottle. Immediately replace the beaker with another of distilled water and then stop the current. Remove the cathode and wash off the water with alcohol. Allow to drain a moment on filter-paper and then dry at about 100° C., cool to room temperature, and weigh. The excess over the original weight of the electrode represents the copper in the weight of ore taken.

It is always a good plan to clean the electrode again with nitric acid, and after igniting and weighing it, replace it once more in the solution and electrolyze for a short time to make certain that all the copper is removed.

The above description will serve very well for those who have to make electrolytic copper assays only occasionally. By means of special arrangements of a less simple nature, including the rapid rotation of one of the electrodes, all the copper in an assay can be satisfactorily deposited very quickly, perhaps in fifteen minutes.

Detailed descriptions of experiments in this direction can be found in the chemical literature of the past few years.

16. Simpler Electrolytic Method.—The main trouble encountered in the electrolytic method is the removal of impurities that might deposit with the copper. The method just described, while accurate, is long and tedious. A much simpler method, which will suffice in most cases, is as follows:

Proceed with 1 gram precisely as in the regular iodide method, removing silver, however, as in **14,** until the washed precipitated copper on the filter is ready to be dissolved in nitric acid. Now remove the filter, wrapping it around the precipitate, and place the whole in a small porcelain crucible. Ignite gently until the paper is consumed and then heat to redness for half an hour or more, avoiding such an intense heat as might melt the oxide of copper formed. Such impurities as arsenic and antimony are to a large extent volatilized. Finally, allow to cool, pour a little nitric acid in the crucible and warm gently until the copper is all dissolved. Transfer the solution to the beaker used for electrolysis, bring to the proper conditions (**15**) and electrolyze as usual.

17. Electrolytic Methods of the Anaconda Copper Mining Co.*—Allow about 0.11 ampere for each determination. With the present arrangements at Anaconda, this gives a tension of from 1.40 to 2.30 volts.

In all cases a drop of the electrolyte is brought in contact with a drop of hydrogen sulphide water, to test if copper has been completely deposited.

The platinum cylinders with deposited copper are washed in water, then alcohol, dried on a steam-bath, and weighed.

If the deposited copper is dark from presence of arsenic, it is dissolved in 8 cc. of nitric acid, diluted with water and electrolyzed again, care being taken to remove from the current soon after the complete deposition of the copper.

Copper may be separated from bismuth, antimony, and arsenic by precipitation as sulphocyanate. The precipitate is washed thoroughly, ignited gently in a porcelain crucible, dissolved in 7 cc. of nitric acid, and the copper is then determined electrolytically.

(*Note by the Author.*—All methods that depend upon the precipitation of copper as sulphocyanate should be avoided for accurate work. I have never found the precipitation to be complete.)

* F. W. Traphagen, Western Chem. and Met., Vol. 6, 192.

In samples containing arsenic, antimony, tellurium, and selenium, such as electrolytic slimes, add 100 mgs. of iron to the nitric acid solution of the sample from which silver has been removed as chloride. Add ammonia to precipitate iron and still have the solution acid. Bring to a boil, settle, filter off the iron precipitate, redissolve it, and again precipitate as before. A third precipitation may be necessary to be certain of having all the copper in solution. Combine the filtrates, evaporate sufficiently, add nitric acid, and electrolyze. The iron precipitate holds the arsenic, antimony, tellurium, and selenium.

Converter Copper.—Dissolve 0.5 gram in 8 cc. nitric acid, 8 cc. water and 1 cc. sulphuric acid, keeping the beaker covered during solution. When solution is complete and the fumes expelled, dilute with water and electrolyze.

In the copper determinations on mattes and converter copper, the percentage of silver, as determined by fire assay, is deducted from the combined percentages of copper and silver found by electrolysis. (291.66 oz. = 1 per cent.) The silver may be precipitated with just sufficient dilute sodium chloride solution, an excess being carefully avoided, and after the silver chloride has been filtered off, the copper may be deposited alone.

Mattes.—Moisten 1 gram of the sample with a few drops of water, add 8 cc. of nitric acid and 1 cc. of sulphuric acid. Run to dryness on steam-bath. Take up with water and 8 cc. of nitric acid. Filter and electrolyze.

Slags.—Decompose 2 grams in a platinum dish with 8 cc. nitric acid, 8 cc. hydrofluoric acid, and 1 to 2 cc. sulphuric acid. Evaporate to sulphuric acid fumes. Take up with water and 10 cc. of nitric acid and electrolyze.

Sulphide Ores.—Weigh 1 gram of the sample into a beaker ($3\frac{1}{2}$ in high and $2\frac{1}{4}$ in. in diameter). Add 8 cc. of nitric acid and a little potassium chlorate. Evaporate to complete dryness on steam-bath. Take up with water and from 6 to 10 cc. of nitric acid. Dilute sufficiently, allow to settle and then electrolyze.

Oxidized Ores.—Take 1 gram of the sample. Evaporate to dryness with 8 cc. of nitric acid. Add 10 cc. of hydrochloric acid and 2 cc. of sulphuric acid, and evaporate to sulphuric acid fumes. Take up with water and 8 cc. of nitric acid, dilute sufficiently, settle, and electrolyze.

18. Rapid Electrolytic Method.—By employing a strong current copper can be deposited very rapidly, but, in the ordinary electrolytic

cell, much of the deposit is then apt to be non-coherent or detached and quite unfit for handling and weighing. This trouble has been overcome by the use of arrangements which rotate one of the electrodes or the electrolyte. These devices are complicated and costly. It has, however, been found that almost equal rapidity may be attained by the use of a specially prepared gauze cathode.* This electrode is made of 52-mesh platinum wire gauze. It is about 1 inch in diameter and $1\frac{1}{2}$ in. long, of cylindrical shape and corrugated and sand-blasted. With 75 cc. of solution and a current of from 8 to 10 amperes and 3 to 4 volts, the copper is usually completely deposited in ten to fifteen minutes. The character of the deposit on the prepared electrode is all that could be desired.

Ores may be treated as described in 14 until the copper, free from interfering elements, is finally obtained in solution as sulphate. Neutralize the excess of sulphuric acid with ammonia, then add an excess of 3 cc. of strong nitric acid, transfer to a tall electrolysis beaker, dilute to 75 cc. and electrolyze with a current of the above strength. The end of the operation may be determined by testing a drop of the electrolyte with a drop of hydrogen sulphide water.

In the absence of interfering elements the process may be greatly simplified, even filtration being omitted when the insoluble residue is slight or settles well. The final conditions, however, as described above, must always be the same, and the solution must be free from chlorides.

Arsenic, if present only in small amount, will not deposit with the copper. Therefore, if the deposited copper is darkened with arsenic, it usually suffices to redissolve it in nitric acid and deposit it once more.

19. Cyanide Method.—In this method the copper is obtained in a blue ammoniacal solution and its amount is estimated from the quantity of standard solution of potassium cyanide required to discharge the blue color. The results of the cyanide titration are exact if certain conditions are always maintained. It is found that for the same amount of copper:

1. A concentrated solution requires more cyanide for decoloration than a dilute solution.

2. A hot solution requires less cyanide than a cold one.

3. In any case when, from a rapid addition of cyanide, the color

* R. C. Benner, Jour. Ind. and Eng. Chem., May, 1910. Benner's electrodes may be obtained of the Denver Fire-Clay Co.

has become rather faint, it may, by simple standing, continue to fade, and perhaps entirely disappear.

4. If the amount of cyanide added is insufficient to effect complete discharge of color, even after allowing the copper solution to stand for several minutes, the titration may then be finished without alteration of the final result.

It is evident from the foregoing facts that in order to obtain correct results the titrations for unknown amounts of copper must be made under conditions that do not differ materially in the following particulars from those governing the standardization of the cyanide solution:

1. Temperature.
2. Rapidity of the final additions of cyanide.
3. Final volume of solution.

Besides the physical conditions just enumerated, there are chemical conditions that affect the result, such as presence of a large amount of chlorides, a large excess of ammonia, etc. Such abnormal conditions require no special consideration, since they are all easily avoided by following the method to be described.

20. Standardization of the Cyanide Solution.—Dissolve pure potassium cyanide in distilled water in the proportion of 21 grams to the liter. Weigh accurately about 0.2 gram of pure copper-foil and dissolve it in an 8-oz. flask in 5 cc. of strong nitric acid (sp. gr. 1.42). Dilute with 25 cc. of water and add 5 cc. of a saturated solution of bromine in cold water. Boil the mixture until the bromine is apparently expelled. Now add 50 cc. of cold water and 10 cc. of strong ammonia (sp. gr. 0.90). Cool to the ordinary temperature by placing under a tap or in cold water. Titrate with the cyanide solution in a slow, cautious manner, and as the end-point is approached, as shown by the partial fading of the blue color, add distilled water so as to bring the volume of the solution to approximately 150 cc. Finish the titration by careful and regular additions of cyanide, finally decreasing to a drop at a time and agitating the flask with a rotary movement after each addition, until the blue tint can no longer be detected by holding the flask against a light-colored background.* It is, of course, very essential that there should be no haste and no prolonged delay in these final additions of cyanide. Simply adopt a regular, natural manner, that can easily be repeated in all subsequent titrations.

* Some operators prefer a porcelain casserole and stirring-rod to a flask.

From the amount of cyanide solution required for the weight of copper taken calculate the value of 1 cc. in copper.

Keep the standard solution in a cool place not exposed to direct sunlight. Under these circumstances it holds its strength fairly well, but still it gets weaker from the decomposition of the cyanide and should be restandardized weekly.

21. Treatment of Ores, etc.—Treat 1 gram, or 0.5 gram if the material seems to contain 40 per cent or over, in an 8-oz. flask with 10 cc. of strong nitric acid. Boil gently until decomposition appears to be complete and then add about 7 cc. of strong sulphuric acid and heat the mixture over a free flame until all the nitric acid is expelled and the residuary sulphuric acid is boiling freely and evolving copious fumes. Remove from the flame and allow to cool. Ores that are not decomposed by this treatment must be attacked in some special manner for which no general directions can be given. Sometimes the addition of hydrochloric acid is all that is necessary. It is advisable in any case not to add the sulphuric acid until the ore appears to be well decomposed.

To the residue in the flask add 20 cc. of cold water and heat the mixture to boiling. If the ore is likely to contain an appreciable amount of silver, add a single drop of strong hydrochloric acid and agitate the liquid so as to collect the silver chloride in clots. One per cent of silver, or 292 oz. per ton of 2000 lbs., will increase the apparent copper contents about 0.29 per cent. Allow to stand, hot, until any anhydrous ferric sulphate is entirely dissolved and then filter, washing flask and filter with hot water. Return the filtrate to the original flask. The volume of the solution should not much exceed 60 cc. at this point. Now place in the flask three pieces of stout sheet aluminum, each about $1\frac{1}{2}$ in. long by $\frac{5}{8}$ in. wide, and heat the mixture to boiling. Boil for perhaps five or ten minutes, according to the volume of the liquid and the appearance of the aluminum. When the copper is all precipitated the aluminum will usually appear bright and clean, or it will become clean by agitating the flask so as to loosen the adhering copper. Remove from the lamp, add about 15 cc. of strong hydrogen sulphide water, which will insure the complete precipitation of the copper, allow to settle a moment, and then decant through a 9-cm. filter, retaining in the flask the aluminum and as much of the copper as possible. Wash the precipitated copper two or three times by decantation with weak hydrogen sulphide water, using about 25 cc. each time and pouring through the filter. Drain the flask as com-

pletely as possible the last time. Now place the flask under the funnel and pour through the latter 10 cc. of a warm mixture of equal volumes of strong nitric acid and water. Do not wash the filter at this point, but remove the flask and replace it with a beaker. Shake the acid about in the flask gently, so as to dissolve all the copper, warming slightly if necessary, but avoid heating more than is required to just dissolve the copper, or the aluminum may be attacked. When solution is complete, pour the entire contents of the flask into the beaker that was placed under the funnel, washing only the lip of the flask, and then pour the solution back into the flask again, retaining the aluminum in the beaker. Wash the aluminum thoroughly and then replace the flask under the funnel. Now pour into the filter 5 cc. of a cold saturated solution of bromine in water, and when it has run through wash the filter with hot water. The bromine is to cleanse any dark sulphur left from the copper sulphide on the filter. In the above operations avoid increasing the bulk of the solution more than necessary. Boil the solution in the flask until the bromine is expelled, then cool somewhat and add 10 cc. of strong ammonia (sp. gr. 0.90) and then continue the cooling to room temperature. Titrate the cool solution with the standard cyanide solution cautiously until the blue color is discharged to a considerable extent and it is evident that the end-point is not far off.

It frequently happens at this point that the liquid is more or less cloudy. When this is the case it should, for accurate work, be filtered. If the titration has been carried too far before filtration, the faint-blue tinge is likely to fade completely away, thus spoiling the assay. On the other hand, if filtered early in the titration, a second milkiness may develop later. Filter the partially titrated solution through a 12.5-cm. filter. One washing will usually suffice. Finish the titration very carefully on the clear, pale-blue solution, precisely as in the standardization previously described. Toward the end dilute if necessary, so as to obtain a final volume of about 150 cc.

The number of cubic centimeters of cyanide solution required, multiplied by the copper value of 1 cc., will give the weight of copper contained in the amount of ore taken, from which the percentage is readily calculated.

None of the ordinary constituents of ores interfere with the method as described.

22. Guess' Electrolytic Method for Ores, etc.—Mr. G. A. Guess observed, in the course of some electrolytic copper work, that a

" nitro " preparation, formed by the action of strong nitric acid on a certain petroleum product, when added to the usual nitric acid electrolyte, permitted the employment of a strong current, with a corresponding shortening of the time of deposition, without injuring the reguline nature of the deposit. Thus the usual period of eight to twelve hours was reduced to three. At the same time it was found that even large amounts of arsenic and antimony did not interfere, and the deposited copper remained bright and uncontaminated.

The following are the details of the method:

*The Nitro Compound.**—Heat very gently a mixture of about 10 grams of vaseline and 100 cc. of strong nitric acid. When all action has ceased, dilute to about 300 cc. and allow to stand for twenty-four hours. After the straw-colored liquid has been filtered, it is ready for use.

The Electrodes.—These are of the Guess-Haultain design and are made of 0.001-in. platinum foil. The cathode is 12.5 cm. long and is divided into a blade 4 cm. wide and 6.25 cm. long, and a central tongue 0.7 cm. wide and 6.25 long, the immersion area being 50 sq. cm. and weight 1.5 grams. The blade is first sand-blasted and then corrugated lengthwise, in order to impart the necessary rigidity. The sand-blasting is to permit a firmer adhesion of the deposited copper, which is otherwise liable to fly off during the final drying.

The anodes are 12.5 cm. long and 0.5 cm. wide with a median corrugation. Three electrodes are used in each cell; one cathode in the middle and one anode on each side of the cathode. These electrodes are connected to slotted aluminum terminals, in which they are held by contact pressure. The terminals are $\frac{5}{8}$-in. rods, projecting 2 in. horizontally in front of the wall of the cabinet; at the back, the middle electrode (cathode) is connected with one pole of the current, and the two outer ones (anodes) with the other pole.

The Procedure.—Weigh the ore into a tall narrow beaker of about 200 cc. capacity, suitable for the electrolysis. Digest with 7 cc. of nitric acid and boil until the red fumes are expelled. Add about $\frac{1}{2}$ cc. of the prepared nitro compound, nearly fill the beaker with water and allow to stand and settle for a moment. Insert the electrodes and electrolyze with a current of 1.5 amperes for three hours.

There should be no evolution of gas whatever at the cathode during the electrolysis. Gas is frequently evolved when the current is first turned on, but if it is turned off for a second and then on again, the

* Modification of Messrs. Cavers and Chadwick, Eng. and Min. Jour., Vol. 89, 954.

bubbles should cease. Gas may again appear at the end of three hours, when the assay is finished.

The cathode with the deposited copper is finally removed, dried, and weighed in the usual manner (15).

23. The Colorimetric Determination of Copper.*—The colorimetric method is applicable only in the case of products containing small amounts of copper, such as slags and tailings. It is based upon the depths of color produced by cupro-ammonium nitrate, and, with proper precautions, it is a delicate and accurate means of determining small percentages of copper. To secure accuracy it is necessary to have the conditions under which the comparison or standard solution was obtained, and that of the sample under examination, as nearly identical as possible. Hence, instead of preparing the standards with known quantities of pure copper only, the various other impurities accompanying the copper in the sample are simulated, by using tailings, blast or reverberatory slags, of known copper content in making up the standard comparison solutions. The following methods are modifications of the method of Thorn Smith. They were developed and are used in the laboratory of the Anaconda Copper Mining Company.

PREPARATION OF STANDARDS

Blast Slags.—Take 3 grams of sample on which the copper has been determined electrolytically, cover with water, add 10 cc. of nitric acid and 1 cc. of hydrochloric acid and heat a few minutes on the steam-bath. Dilute the mixture, after heating, with 100 cc. of water, add dilute ammonia in slight excess and filter into a colorimetric bottle. Wash until the filtrate fills the bottle to the mark. If the electrolytic copper on this sample was 0.20 per cent. this standard is called "B–2." To prepare "B–3" add 0.003 gram of copper to another 3 grams. "B–4" is prepared by the addition of 0.006 gram of copper, and "B–5" by adding 0.009 gram of copper, the copper being always added before the ammonia, and the samples treated as in the preparation of "B–2." If samples low enough in copper to prepare the lowest standards are not at hand, all the copper may be removed electrolytically and then sufficient of a standard copper solution added for the required standard.

Tailings.—Heat 1 gram of the sample on the steam-bath with 5 cc. of nitric acid and a pinch of potassium chlorate. Dilute, filter and

* From papers by F. W. Traphagen, Western Chem. and Met., VI, 148, and Arthur Austin, Western Chem. and Met., VI, 309.

wash as for slags. If the electrolytic copper on this sample was 0.50 per cent, the standard is called " T–5." To prepare " T–6 " add 0.001 gram of copper to another gram sample; 0.002 gram for " T–7 "; 0.003 gram for " T–8 "; 0.005 gram for " T–10."

Reverberatory Slags.—Take 2 grams of sample, add 10 cc. of hydrochloric acid and 2 cc. of nitric acid. Heat, dilute, add ammonia, filter and wash as for blast slags. If the electrolytic copper on this sample was 0.30 per cent, this standard is called " R–3." For " R–4 " add 0.002 gram of copper to another 2 grams of sample. Add 0.004 gram for " R–5," 0.006 for " R–6," and so on. Treat each as in the preparation of " R–3."

A set of standards being prepared as above, another set of bottles is arranged, each bottle being filled almost to the mark with water and 10 cc. of ammonia. A standard solution of copper, containing 0.001 gram of copper to the cubic centimeter, is run into each from a burette until the color produced exactly matches a corresponding standard prepared as above. The burette reading is carefully noted in each case.

The following results were thus obtained:

B–2	required	4.4 cc.	R–2	required	3.2 cc.	T–3	required	2.8 cc.
B–3	"	6.7 cc.	R–3	"	4.6 cc.	T–4	"	3.8 cc.
B–4	"	9.1 cc.	R–4	"	6.1 cc.	T–5	"	4.7 cc.
B–5	"	11.1 cc.	R–5	"	7.9 cc.	T–6	"	5.7 cc.
			R–6	"	9.7 cc.	T–7	"	6.6 cc.
			R–7	"	11.4 cc.	T–8	"	7.6 cc.
			R–8	"	13.2 cc.	T–9	"	8.5 cc.
						T–10	"	9.5 cc.

By the use of this table standards may be rapidly prepared.

Determination of Copper

Treat blast slags, reverberatory slags and tailings exactly as described in " Preparation of Standards " and match the filtrates with the standards.

Details of Operation.—Except in the case of converter slag (of which 0.5 gram is taken) all portions are 1, 2, or 3 grams.

Tailings are weighed into No. 1 beakers, 100 cc. capacity, and slags into No. 2 beakers, 200 cc. capacity.

Tailings are treated with nitric acid and a pinch of potassium chlorate, set upon the steam-plate and left for half an hour. The addition of nitric acid should be regulated so as to leave about 5 cc. after treatment on the hot plate. After the hot plate treatment about 25 to 30 cc. of cold water are added to the beakers and they are then placed in front of the color bottles which have been previously arranged. These color bottles are of square shape, to allow of easy and safe

handling, and are made of clear white glass. They are $7\frac{1}{2}$ in. high, with a body $2\frac{1}{2}$ in. in diameter and a short neck about $1\frac{3}{4}$ in. in diameter. Ammonia (1 : 1) is added to the beakers in such quantity as to give about the same excess as is used in the standards. Ribbed funnels $4\frac{1}{4}$ in. in diameter are set in the mouths of the bottles, and provided with filters $18\frac{1}{2}$ cm. in diameter. The contents of the beakers are now poured "clean" into the filters. The beakers are washed once with warm water, which is then poured through the filters, and, after draining, the precipitate in each filter is given one good wash with warm water. The funnels are now removed and the bottles are filled up to the standard marks with water. The larger bulk of solution before filtering and the greater amount of wash water required cause the mark on the slag bottles to be higher than that on the tailings. On the bottle described the tailings mark will come about halfway up, and the slag mark will be near the top. The tests, when ready, are matched against the standard colors arranged in a color stand. The latter is made of wood, painted white, and faces a window. Each standard bottle is in a separate compartment, so as not to be affected by the color of an adjacent standard. In making comparisons the standard and the unknown should be at equal distances from the partitions, as the latter have a slight effect on the color.

Results are read and reported to the nearest 0.05 per cent by reading between the standards, which are graduated to 0.1 per cent.

Blast slags decompose easily; reverberatory slags are best decomposed by first adding hydrochloric acid, and then, after a few minutes' digestion, adding nitric acid. Add a little water before the acid, so as to make a paste, which will prevent caking.

Reverberatory and converter slags should be allowed about three-quarters of an hour on the steam-plate, and, when taken up with water, stir thoroughly with a rubber "policeman." The dilute ammonia should be added while stirring, so as to best judge the required excess.

Sometimes the color produced in a test has a greenish tinge, and the test is then apt to be read too high. Heath states that this may be due to the presence of organic matter, which impairs the complete precipitation of ferric hydroxide by ammonia. If the green tint is too pronounced the sample should be ignited.

Standards of low copper content seem to preserve their color best with a small excess of ammonia, 5 cc. Those of higher copper content require 10 to 20 cc. excess. The sample to be matched should be as nearly like the standard in all respects as possible.

CHAPTER XIV

FLUORINE

1. Norris' Method for the Determination of Fluorine in Fluorspar and Ores.*—Special reagents required:

Standard Calcium Acetate Solution.—Dissolve 13.16 grams of pure calcium carbonate in a mixture of 100 cc. of glacial acetic acid and 100 cc. of water and dilute to 1 liter. Standardize by determining the CaO in 30 cc., titrating the oxalate precipitate with the standard permanganate, and then, from the formula CaF_2, calculate the percentage value of 1 cc. in fluorine on the half-gram basis. Should equal about 1 per cent.

Standard Potassium Permanganate Solution.—8.316 grams per liter. Standardize against about 0.7 gram of pure sodium oxalate. Calculate for CaO per cubic centimeter and then for the value of 1 cc. in the standard calcium acetate solution.

Sodium Oxalate Solution.—17.62 grams per liter. Not standardized, but 1 cc. will correspond to about 1 cc. of the calcium acetate solution.

Silver Nitrate Solution.—Dissolve 5 grams of silver nitrate in water and dilute to 100 cc.

Sodium Chloride Solution.—Dissolve 5 grams of pure sodium chloride in water and dilute to 100 cc.

Procedure.—Bring to a quiet fusion 5 grams of potassium hydroxide and 3 grams of sodium carbonate in a thin spun-iron crucible of about 25 cc. capacity.[1] Remove from the heat, allow to cool partially, and add 0.5 gram of the finely ground material and 0.5 gram of finely ground silica. Cover the crucible with a very loosely fitting porcelain or iron cover, bring the mass to quiet fusion and maintain at that point for twenty-five or thirty minutes.[2] Remove the cover and pour the melt on a cold iron plate, covering with an evaporating dish to prevent loss from violent cracking on cooling.

Have ready a 500-cc. beaker containing about 1½ in. of cold water. Place the crucible in this, after pouring, and heat to remove adhering

* Dr. W. V. Norris, Colorado School of Mines,

melt, then lift it out with a glass rod, wash and remove it. The cover may be similarly treated, or perhaps simply washed clean with a jet of hot water. Now place the cold melt in the beaker and boil for about five minutes to effect complete disintegration.[3]

Filter the mixture, using a filter plate set in a loop funnel and having the filter paper covered with a layer of asbestos fiber. Wash ten times with hot ammonium carbonate solution; 5 grams in 100 cc.[4] Receive the filtrate in a large beaker.

(Silica may now be removed as follows, but its removal is apparently unnecessary: Add 10 grams of ammonium carbonate, cover, heat (cautiously) to boiling and boil until the odor of ammonia is gone, or nearly so. Filter through a filter similar to the last and wash ten times with hot water. This removes nearly all the silica.)

Whether the silica has been removed or not, proceed as follows:

Acidify almost exactly with acetic acid and then add an excess of glacial acetic acid in the proportion of 1 cc. to every 100 cc. of solution. Now, from a burette, add a measured amount of the standard calcium acetate solution, which should be in excess relative to the possible fluorine present, but not exceeding 50 cc. in any case. Boil for five minutes, then remove from the heat, cool and transfer to a 1000-cc. measuring flask. Make up to the mark with cold water, mix and then allow to settle for about half an hour.[5] Fill a 500-cc. measuring flask up to the mark with the clear liquid. Transfer this to a large beaker, through a filter, if necessary, and washing the filter ten times with small portions of hot water. Add 35 cc. of the sodium oxalate solution, boil ten minutes and then filter, washing ten times with hot water.

Make a mixture of 200 cc. of water and 10 cc. of strong sulphuric acid in a beaker. Heat nearly to boiling, add the filter and precipitate and titrate with the standard permanganate to the usual pink tinge.

Calculate the cubic centimeters of permanganate used to the equivalent amount of calcium acetate solution. Deduct this from the total amount of calcium acetate solution taken, bearing in mind, however, that the solution was divided before precipitation, and therefore only one-half the original amount of calcium acetate solution is under consideration. The remaining calcium acetate solution, multiplied by 2 and then by its percentage factor for fluorine, will give the percentage of fluorine in the substance.[6]

[1] This is to expel water that would otherwise cause much spattering.

[2] This fusion may sometimes seem unnecessarily long, judging from the appearance of the melt; but experience has shown that an apparently clear melt is not a safe guide and that it is not advisable to shorten the time prescribed.

[3] All the fluorine should now be in solution as alkali fluoride. The calcium will exist as carbonate.

[4] The ammonium carbonate is to lessen the danger of dissolving some of the calcium carbonate.

[5] Settling is resorted to because the precipitated calcium fluoride filters very badly.

[6] The calcium acetate solution, prepared by dissolving 13.16 grams of $CaCO_3$ per liter in acetic acid, will contain the equivalent of 7.3732 grams of CaO per liter, or 0.007372 gram per cubic centimeter. One CaO is equivalent to CaF_2, or, F_2. That is, 56.07 parts by weight of CaO = 38 parts of F. The weight of CaO in 1 cc., 0.007372 gram, will accordingly correspond to 0.005 gram of F, or 1 per cent on the half-gram basis.

Two $KMnO_4$, molecular weight 316.06, contain 5 available oxygen atoms. Each CaO, molecular weight 56.07, determined as oxalate, is equivalent to 1 oxygen. Five oxygen, or 316.06 parts by weight of permanganate, will therefore equal 280.35 parts of CaO. If the permanganate solution is made exactly 8.316 grams per liter, 1 cc. will contain 0.008316 gram. By proportion, this will correspond to 0.00737 gram of CaO, or, 1 cc. of the calcium acetate solution. If standardization shows that the calcium acetate and permanganate solutions vary in strength from the theoretical, calculate their exact values and mutual relations in accordance with the above.

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2. Rapid Practical Method for Fluorspar.—Take 0.5 gram of the ore in an 8-oz. flask, moisten with water, add 5 cc. of glacial acetic acid and boil nearly to pastiness. Take up in about 50 cc. of dilute acetic acid (1 acid to 2 water) and boil gently for a few minutes. These operations will not affect calcium fluoride, but will usually extract practically all other calcium salts. Filter, washing well with hot water. Place about 3 grams of powdered anhydrous sodium sulphate in a small platinum dish, mixing in also a little potassium nitrate, if reducible metals are likely to be present. Lay the filter and residue upon this mixture and ignite gently until the paper is burned fairly well. Now cool and add 5–6 cc. of strong sulphuric acid. Heat carefully, to avoid spattering, first to strong fumes, and then to a melt, if possible. If the mass solidifies at the end, without melting, cool sufficiently, add a little more sulphuric acid and heat again. This will usually effect complete decomposition of the fluoride, and expulsion of the fluorine, even if the mass is not completely melted. Allow

to cool, cover the dish and dissolve the cake by warming with sufficient water acidulated with 5 cc. of hydrochloric acid. Transfer the solution to the original flask, first filtering, if there is an appreciable amount of insoluble residue. Dilute to about 150 cc. with hot water and proceed with the determination of CaO as described in CALCIUM, 1, at the same point. Multiply the percentage of CaO found by 1.393 to obtain the percentage of CaF_2.

3. Valuation of Fluorspar. Method of Dr. Bidtel.*—The usual determinations are calcium carbonate, silica and calcium fluoride, although other constituents are sometimes required.

Calcium Carbonate.—Place 1 gram of the finely powdered sample in a small Erlenmeyer flask, add 10 cc. of 10 per cent acetic acid and insert a short-stemmed funnel in the neck of the flask as a splash trap. Heat the mixture for one hour on a water-bath, agitating from time to time. The calcium carbonate is decomposed and may be dissolved out as the soluble acetate, while calcium fluoride and silica are practically unaffected. Filter the solution through a 7-cm. ashless filter and wash the residue four times with warm water. Ignite filter and contents in a weighed platinum crucible at as low a temperature as will completely burn the filter. The loss of weight minus 0.0015 gram (the amount of calcium fluoride soluble in acetic acid under the conditions named) is reported as calcium carbonate.

Silica.—Mix the residue in the platinum crucible with about 1 gram of yellow mercuric oxide, in the form of an emulsion in water, breaking up any hard lumps that may have formed. Evaporate the mixture to dryness, heat to dull redness, then cool and weigh. The mercuric oxide oxidizes any sulphide that may be present. Add about 2 cc. of hydrofluoric acid and evaporate to dryness. Repeat this process twice (performing it three times in all), to ensure complete expulsion of silica (as SiF_4). Now add a few drops of hydrofluoric acid, a little macerated filter-paper and then a few drops of ammonium hydroxide, to precipitate the iron. Evaporate to dryness, ignite to dull redness, cool and weigh. Report the loss from the previous weighing as silica.

Calcium Fluoride.—Treat the residue with 2 cc. of hydrofluoric acid and 10 drops of nitric acid (to decompose the oxides), cover the crucible and place on a moderately warm water-bath for thirty minutes. Now remove the lid and evaporate to dryness. Repeat the

* Dr. E. Bidtel, Jour. Ind, Eng. Chem., Vol. 4, p. 201; Vol. 6, p. 265.

evaporation with hydrofluoric acid to ensure the transposition of the nitrates to fluorides. If the residue is still colored, repeat the evaporation a third time. Finally, add a few drops of hydrofluoric acid and 10 cc. of ammonium acetate solution. The acetate solution is made by neutralizing 40 cc. of 80 per cent acetic acid with strong ammonia, adding 2 grams of citric acid and making the mixture up to 100 cc. with strong ammonium hydroxide. Digest the mixture in the crucible for thirty minutes on a boiling water-bath, then filter, washing first with water containing a small amount of ammonium acetate, and finally with pure hot water. (Several washings by decantation are advisable.) Ignite the residue in the same crucible as before and weigh as calcium fluoride. To this weight add 0.0022 gram to compensate for loss of CaF_2.

Pure calcium fluoride is white. To test the purity of the residue, add 2 cc. of sulphuric acid and heat to fumes to decompose the fluoride, then add an additional cubic centimeter of sulphuric acid and heat to complete dryness, expelling all the free acid. Weigh the residue as calcium sulphate, which, on calculation, should check the calcium fluoride previously weighed. Now fuse with sodium carbonate and treat the mass, after cooling, with dilute hydrochloric acid in excess. If barium is present the solution will be cloudy from barium sulphate.

CHAPTER XV

IRON

1. In the determination of iron in ores and metallurgical products some modification of either the permanganate or dichromate volumetric method is ordinarily employed. Both methods give exact results, and the choice of the one to use usually depends on either the personal preference of the operator or the convenience of the case in hand.

The following modifications of these methods are employed in my laboratory.

2. **Permanganate Method.**—This method is based on the following reaction:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

The ferrous salt, which may be either a sulphate or a chloride, is oxidized to the ferric condition by the permanganate, which is itself decomposed and decolorized. When the permanganate in solution is added gradually, its color is continually destroyed as long as any ferrous salt remains, but as soon as the oxidation is complete the addition of more permanganate imparts a permanent pink tint to the liquid. The above equation shows that it requires 316.06 parts of potassium permanganate to oxidize 558.4 parts of iron from the ferrous to the ferric condition. To make a standard solution, therefore, so that 1 cc. shall equal 1 per cent of iron, i.e., 0.005 gram when 0.5 gram of ore is taken for assay, we solve the proportion

$$316.06 : 558.4 = x : 0.005.$$

$x = 0.00283$.[1] This is the weight of permanganate required in 1 cc., which is equivalent to 2.83 grams per liter. When used for iron determinations, the solution may conveniently be made of approxi-

mately this strength. Its exact value is determined by standardization.

3. There are three common methods of standardizing the permanganate solution:

1. By metallic iron or an iron solution of known strength.
2. By a stable ferrous salt.
3. By oxalic acid or an oxalate.

I have found the metallic iron method, when carried out as described below, and the oxalic acid or oxalate method to give practically identical results, and I ordinarily use the latter on account of its simplicity. The stable ferrous salt usually employed is ferrous ammonium sulphate. As ordinarily obtainable it is not a sufficiently reliable basis for the best work.

After the permanganate solution has been made up it should be allowed to stand at least a day before standardizing, as when first prepared it is constantly changing in strength, owing to oxidation of the organic matter always present in the liquid.

4. To standardize by means of metallic iron, weigh 0.15–0.20 gram of very finely drawn clean iron wire and dissolve in an 8-oz. flask in a mixture of 5 cc. each of strong nitric and hydrochloric acids.

Very finely drawn polished iron wire can be purchased at the supply stores marked with its true percentage of iron, usually about 99.8. Sutton recommends the use of soft " flower-wire," of which the actual percentage of iron may be assumed to be 99.6. Pure electrolytic iron in granulated form is also to be obtained. It has the advantage of dissolving very rapidly in hydrochloric or dilute sulphuric acid, and is said to keep well without oxidizing. When iron wire is used the precaution should be taken to have it perfectly clean and free from rust. If polished and apparently clean, it may simply be drawn through a piece of filter-paper held in the hand to insure freedom from dust and grease, but if at all oxidized it should first be thoroughly cleaned with fine emery-paper or cloth.

5. Having placed the wire in the flask, best in a snug coil, add the acid and warm the mixture gently. The wire will quickly dissolve. Besides effecting a rapid solution of the iron, the aqua regia also serves to oxidize hydrocarbons and other compounds, due to impurities in the wire, that would otherwise consume a little permanganate in the titration. When the wire has dissolved add 5 cc. of strong sulphuric acid and boil over a free flame (manipulating the flask in a holder)

until the hydrochloric and nitric acids are expelled and most of the sulphuric also. Allow to cool and add 30 cc. of cold water, 10 cc. of strong hydrochloric acid and 3 cc. of 4 per cent $CuSO_4$ olution.*

6. Now add 6 grams of pure granulated zinc (best about 20-mesh). This should be roughly weighed, as all zinc contains a little iron and the error thus introduced must be subsequently determined and allowed for. The iron is reduced from the ferric to the ferrous condition according to the equation

$$2FeCl_3 + Zn \rightarrow 2FeCl_2 + ZnCl_2.$$

Hydrogen is also liberated by the action of the free acid on the zinc. The copper added precipitates arsenic.

Allow the reaction to continue until the solution is completely decolorized, heating, if necessary, toward the end if the action is slow. Now add 50 cc. of cold water to the mixture in the flask, and then 10 cc. of strong sulphuric acid. This will dissolve whatever zinc remains and will also supply the solution with a large excess of sulphuric acid. The latter will counteract the otherwise disturbing influence of the hydrochloric acid present during the subsequent titration and secure a sharp end-point. Hydrochloric acid and potassium permanganate mutually decompose each other with the evolution of chlorine as follows:

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 10Cl.$$

When this takes place during an iron titration, the amount of permanganate consumed is increased, thus producing high results, while the end-point is obscured owing to the continual fading of the pink tinge. If, however, the solution is cold, largely diluted, and contains a proper excess of sulphuric acid, a little hydrochloric acid causes no trouble.†

7. When the zinc is nearly all dissolved the mixture should be filtered. Nearly all zinc contains lead as an impurity, and this remains behind as a finely divided black residue, which would cause trouble by consuming permanganate if not filtered off. As the solution has a

* It is a good plan to make this solution slightly ammoniacal and subsequently filter off any $Fe_2(OH)_3$.

† It appears to make a very slight change in the standard, but this is of no consequence in technical work, as iron determinations are made the same way.

tendency to clog a filter and run very slowly it is better to filter through a plug of absorbent cotton placed in a funnel and moistened. Do not use an unnecessarily large wad. Place it in the funnel so that the under side is smooth, with the fibers lying horizontally. If the latter are allowed to string downward they are liable to obstruct the neck of the funnel and cause a slow filtration. The proper arrangement filters rapidly and washes easily. Receive the filtrate in a 4-inch by 5-inch glass battery-jar containing an inch or two of water. Wash the filter and residue well with cold water.

8. Dilute the solution in the battery-jar with cold distilled water to about 700 cc., having previously placed a mark on the jar at that point. The solution is now ready for titration, which should proceed without unnecessary delay, to avoid oxidation of the ferrous iron by the air. Place a piece of white paper under the jar, in order that the color change may be rendered more distinct, and run in the permanganate solution from a burette while stirring the mixture with a glass rod. The color of the permanganate is almost instantly destroyed at first, but as the end-point is approached a less rapid decolorization can easily be detected if the permanganate be added cautiously. Proceed more and more carefully, finally drop by drop, until a very faint permanent pink tinge is obtained. The reaction being now complete, read the burette. Another drop of permanganate should turn the solution decidedly pink.

Before calculating the standard of the permanganate it is necessary to apply a correction by deducting the amount of permanganate solution required to produce the same pink tint in a solution containing no dissolved iron wire, but otherwise of the same volume and condition and containing the same reagents. To determine this correction once for all for the same reagents, proceed as follows:

9. Treat 6 grams of the zinc regularly used, in an 8-oz. flask, with a mixture of 10 cc. of strong hydrochloric acid, 25 cc. of water and 3 cc. of 4 per cent $CuSO_4$ solution. Add gradually a mixture of 10 cc. of strong sulphuric acid and 20 to 30 cc. of water. When the zinc has about all dissolved, dilute with cold water and filter through absorbent cotton as described for the standardization, finally titrating with permanganate precisely as before. Note the amount of permanganate required and deduct this volume from the burette reading of all corresponding iron titrations.

A correction is sometimes made for the color due to the ferric

salt present at the end of a titration, but the error from this cause is usually negligible.

10. Having now, in the standardization of the permanganate, taken the final reading of the burette and deducted the correction, there remains only to divide the actual weight of iron in the iron wire taken by the number of cubic centimeters used to find the value of 1 cc. in iron.

Example.—Weight of iron wire taken..... 0.1725 gram
Actual weight of iron (99.8%)..... 0.1721 "
Burette reading.....34.90 cc.
Correction..... 0.20 "

Corrected reading.. .....34.70 cc.

$0.1721 \div 34.70 = 0.004961$.

This is the weight of iron in grams to which 1 cc. of the permanganate is equivalent.

On the basis, then, of 0.5 gram of ore being taken for assay, 1 cc. = 0.9922 per cent of iron.

11. To standardize by means of a ferrous salt, ferrous ammonium sulphate is commonly used. This salt has the composition $FeSO_4(NH_4)_2SO_4+6H_2O$. It contains 14.24 per cent of iron, although it is frequently assumed to contain exactly one-seventh of its weight of iron. Weigh from 1 to 1.5 grams of the pure salt (the usual C. P. article is seldom of the theoretical composition) and dissolve in a battery-jar in 700 cc. of cold distilled water acidified with 10 cc. of strong sulphuric acid. Titrate at once to the usual pink tint. Make a blank test on the plain acidulated water to determine the amount of permanganate required to produce a tint and deduct the correction thus found from the former reading. Calculate the standard as above.

12. To standardize with oxalic acid, proceed as described in CALCIUM, **6**, and determine the oxalic value of 1 cc. of the permanganate. This value multiplied by 0.8855 will give the iron factor. Sodium oxalate,* (Sorensen's salt), sold for standardizing, is to be preferred to oxalic acid, as of more certain purity. It is treated in the same way as oxalic acid. The sodium oxalate value of the permanganate multiplied by 0.8332 will give the iron value. This is a

* $Na_2C_2O_4$.

convenient and accurate method and is the one usually employed in my laboratory.

13. Treatment of an Ore.—Weigh 0.5 gram of the ore and place in an 8-oz. flask. Decompose with acids according to the nature of the sample. It is usually best to begin with 10 cc. of strong hydrochloric acid and warm gently as long as decomposition appears to progress, adding more acid if necessary. If undecomposed sulphides remain, add 5 cc. of strong nitric acid and continue the heating. Note whether the insoluble residue now appears white or discolored. In the latter case endeavor to effect a better decomposition by continued gentle heating with hydrochloric acid. Finally, add to the mixture (which should not be so concentrated as to contain separated salts) about 5 cc. of strong sulphuric acid and heat the flask, supported in a holder, over a free flame until practically all the acid, including the sulphuric, is expelled.* Allow to cool, add 30 cc. of cold water and 10 cc. of strong hydrochloric acid, and the mixture is at once ready for the reduction of the iron with zinc. It is not necessary to get the salts into solution before adding the zinc. They will dissolve very quickly after reduction begins.

If hydrochloric acid alone effects a solution of all the iron in the ore, the further treatment with nitric or sulphuric acid is unnecessary. In such a case, in order to have the right amount of acid finally present, boil the solution nearly to dryness and then add 8 cc. more of hydrochloric acid. Dilute to 40 cc. with cold water and proceed with the reduction.

14. Add 6 grams of pure granulated zinc (20-mesh) and reduce the iron precisely as described for the standardization of the permanganate by the metallic iron method (**6**).

When the reduction is complete, dilute with 50 cc. of cold water and then, with a little caution, add 10 cc. of strong sulphuric acid. Besides a residue of lead from the zinc itself, reducible metals from the ore, such as lead, copper, arsenic, etc., will be precipitated. All this residue must be removed. When the zinc is nearly all dissolved filter the mixture through a plug of moistened absorbent cotton into a battery-jar, as described in **7**, washing the filter well with cold water. Dilute to 700 cc. and titrate at once with permanganate, as described in **8**. After reading the burette, deduct the correction previously determined

* Nitric acid may not be entirely expelled by this treatment unless all nitrates are in solution when the sulphuric acid is added.

(9) and multiply the actual number of cubic centimeters used for the ore by the percentage value of 1 cc. for iron. This gives the percentage of iron in the sample.

15. Effect of a Large Amount of Arsenic.—Ores containing a large amount of arsenic will frequently give low and variable results, and the titration will have a rather quickly fading end-point. Apparently, some arsenic has been left in solution, after the reduction, in the *ic* condition, and this, by subsequently oxidizing iron, brings the results low, as the arsenious acid produced is only very slowly acted upon by the permanganate. The addition of cupric sulphate solution, as prescribed in 5, usually prevents this trouble by precipitating metallic copper on the zinc, which in turn precipitates the arsenic as copper arsenide. The zinc alone cannot be depended upon to do this.

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[1] Calculations of this kind may be greatly simplified without considering extended reactions. Potassium permanganate is an oxidizing agent, with the formula $KMnO_4$. The latter may be written $K_2Mn_2O_8$, or $K_2O.Mn_2O_7$, the molecular weight of which is 316.06. The oxidizing portion of this compound is the Mn_2O_7, which, by giving up O_5, is reduced to Mn_2O_2, or, $2MnO$, the Mn changing its apparent valence of 7 to 2. The main point to be considered is that every $K_2O.Mn_2O_7$ has 5 available oxygen atoms. Now, when ferrous iron is oxidized, the reaction, without regard to the actual combination of the iron, may be considered simply as a change from FeO to Fe_2O_3, as follows: $2FeO$, or Fe_2O_2, $+O = Fe_2O_3$. This shows that every Fe_2 requires 1 oxygen, or, $O = Fe_2$. The two points thus established, and which should be remembered in volumetric work, are that $K_2O.Mn_2O_7 = O_5$, and that $O = Fe_2$. It now follows that $K_2O.Mn_2O_7 = 10Fe$, that is, 316.06 parts by weight of the permanganate = 558.4 parts of Fe.

While the above explanation may appear long, the actual work required in a calculation made by this method is comparatively small, as it obviates the necessity of writing out long reactions.

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16. Treatment of Silicates and Other Refractory Substances.—The acid treatment just described will serve excellently for the decomposition of most ores treated at western lead-smelters, but silicates, furnace products, refractory oxides, etc., are frequently encountered that do not thus yield up all their iron. In the purchase of ores for lead-smelters the actual total iron contents are not, as a rule, absolutely required, but only what is obtained by the acid treatment. In the majority of cases practically all the iron is thus dissolved. What remains is classed with the insoluble residue or "silica." Whenever the total iron is required the material must, of course, be completely decomposed.

17. Method that is Frequently Effective when Acids Fail.—Weigh 0.5 gram of the finely ground material into an 8-oz. flask. Add 5 grams of dry sodium sulphate and about 6 cc. of strong sulphuric acid. Manipulate the flask in a holder over a strong naked flame, boiling off all the acid and finally reducing the residue to a nearly or actually red-hot melt. Do this final heating with the melt on the side of the flask, so as not to bulge the bottom. Cool with the flask on its side, in order that the contracting cake will not crack it, or, distribute the melt around the sides of the flask until it solidifies. This treatment will effect a complete decomposition of many refractory ores, either sulphides or oxides. Silicates may not be much attacked. If undecomposed particles remain that are likely to contain iron, the following procedure may be tried: Add 10 cc. of water to the cooled mass and about 6 cc. of sulphuric acid. Heat until the cake has dissolved or disintegrated, then add hydrofluoric acid, about as much as can be held in an ordinary platinum crucible cover, and repeat the previous treatment over a naked flame. The flask will not be materially attacked and the glass is not likely to contain iron in sufficient amount to affect the determination. If this treatment still leaves a dark insoluble residue, one more effort may be made on the same portion. To the cool mass add water and sulphuric acid and disintegrate as before. Now add one-eighth of a 9-cm. filter paper and again run down over the flame until the carbon is all burned off and a melt once more obtained, then cool as before. Antimonial compounds will frequently yield to this treatment (owing to the reduction of the antimony to the *ous* condition) where the other methods fail. Of course this last method, combined with hydrofluoric acid also, may be tried at the outset, but in practice I have usually found the extra steps unnecessary.

If a satisfactory decomposition has been attained, add 30 cc. of water and 10 cc. of hydrochloric acid to the cool mass and warm gently to dissolve the cake. Continue from this point as described in **14**.

18. Refractory Silicates.—Silicates, or mixed material containing silicates, may be decomposed as described under SILICA. The nature of the material has to be considered in deciding upon the best course to pursue and the matter of the decomposition is fully explained in the section referred to. An acid solution of the iron is thus finally obtained. If in two portions, as the result of an acid treatment followed by a fusion of the residue, they should be united. When only iron is to be determined it is usually unnecessary to evaporate to dryness to remove

silica. Warm the solution in a beaker, add a little bromine water if the iron is not fully peroxidized, and then precipitate the iron as ferric hydroxide with excess of ammonia. Heat to boiling, allow to settle, filter, and wash thoroughly with hot water. With a jet from the wash-bottle transfer the bulk of the washed precipitate from the filter to a beaker, using as little water as possible, and then place the beaker under the funnel. Pour through the filter a hot mixture of 10 cc. of strong hydrochloric acid and 10 cc. of water, so as to dissolve the precipitate still remaining, finally washing the filter with a little hot water. Warm the mixture in the beaker to dissolve all the ferric hydroxide, concentrate if necessary, by boiling, to about 30 cc., and transfer the solution to an 8-oz. flask. Reduce with zinc and continue in the usual manner, as directed in **14**.

19. Decomposition of Silicates by Hydrofluoric Acid.—Sometimes the iron in a silicate, or a silicious residue remaining after acid treatment, can be quickly dissolved as follows:

Treat the substance in a small platinum dish with equal parts of strong pure hydrochloric and hydrofluoric acids. Warm gently until decomposition appears complete, adding more of the acids if necessary, and then add about 3 cc. of dilute sulphuric acid (1 : 2) and evaporate to white fumes. To the cool residue add a little water and a few drops of hydrochloric acid and warm to effect solution. If the material is a residue, transfer this solution to the flask containing the original filtrate, make to a volume of about 40 cc., reduce with zinc, and finish as usual (**14**). If the material is the ore itself the operations are similar but 5 cc. of hydrochloric acid must be added before reduction. When nitric acid has been used in a preliminary treatment it should be expelled before filtration from the residue (**13**). The solution for reduction should have a volume of about 40 cc. and contain from 5 to 10 cc. of free hydrochloric acid.

20. Titaniferous Ores.—In case an ore contains an appreciable amount of titanic acid it becomes impracticable to use zinc as a reducing agent, since the TiO_2 in solution is thereby reduced to Ti_2O_3 (which imparts a purple or blue color to the liquid), and the latter is subsequently oxidized back to TiO_2 again by the permanganate. Thus more permanganate will be required than corresponds to the amount of iron present.

With such titaniferous ores proceed according to **17**, **18** or **19**, as appears most suitable for the case in hand, until the final solution is

obtained in the flask ready for reduction. The volume should be about 40 cc. Cautiously add enough ammonia to produce a slight permanent precipitate of ferric hydroxide which persists even after vigorous shaking. Now add 5 cc. of a strong solution of ammonium acid sulphite,* shake well, and then warm the flask gently. Ferric iron is reduced, while titanic acid remains unaffected. As the deep-red color fades, increase the heat gradually to the boiling-point. When quite colorless, add a mixture of 10 cc. of strong sulphuric acid and 20 cc. of water and continue the boiling until all odor of sulphur dioxide has disappeared. Now place the flask in cold water and add cold water until the flask is nearly full. When the solution is quite cold, transfer it to a battery-jar, dilute to 700 cc., and titrate with permanganate as usual (8).

21. **Chrome Iron Ore.**—Treat as described in CHROMIUM, 2, except that a nickel or copper crucible must be used instead of an iron one. After the chromium is filtered off, the iron is left with the residue on the filter as ferric hydroxide. With as little hot water as possible rinse the residue from the filter into a small beaker. Place the latter under the funnel and dissolve whatever precipitate still adheres to the filter by slowly pouring through the latter a warm mixture of 10 cc. strong hydrochloric acid and 15 cc. water. Heat the mixture in the beaker to dissolve all the ferric hydroxide and then transfer to an 8-oz. flask, reduce with zinc, and determine the iron according to 14.

22. **Zimmerman-Reinhardt Method as Modified by Mixer and Dubois.**†—This modification of the permanganate method is extensively used in the Lake Superior region for the rapid determination of iron in the oxidized ores of that section.

The following solutions are required:

Stannous Chloride.—Dissolve 1 lb. of stannous chloride in 1 lb. of strong hydrochloric acid (1.2 sp. gr.) to which some water has been added, and dilute to 2 liters.

Hydrochloric Acid of 1.1 *Sp. Gr.*—Mix equal volumes of the strong acid (1.2 sp. gr.) and water.

Mercuric Chloride.—Make a saturated solution in hot water, allow to cool and crystallize, and then filter.

* Ammonium acid sulphite may be made by passing sulphur dioxide into strong ammonia water until the liquid becomes yellowish and smells strongly of sulphur dioxide. An old solution always contains some thiosulphate which will give a precipitate of sulphur with ferric salts.

† Jour. Am. Chem. Soc., XVII, 405.

Manganese Sulphate.—Dissolve 160 grams in water and dilute to 1750 cc. To this add 330 cc. of phosphoric acid syrup of 1.7 sp. gr. and 320 cc. of sulphuric acid, 1.84 sp. gr. This solution is to obviate the deleterious action of liberated chlorine when potassium permanganate is added to a hydrochloric acid solution containing ferrous iron.[1] The phosphoric acid allows the formation of iron phosphate, which, being nearly colorless, renders the end-reaction more distinct.

23. Treatment of an Ore.—Treat 0.5 gram in a small covered beaker with 2.5 cc. of the stannous chloride solution and 10 to 15 cc. of the dilute hydrochloric acid. Boil the mixture very gently on an iron plate until the ore is completely decomposed. For ores running less than 55 per cent of iron it is advisable to use a little less stannous chloride. The solution of the ore is usually very rapid, requiring only a few minutes.

When the ore is dissolved, run a few drops of stannous chloride from a burette into the hot solution until all the iron is reduced to the ferrous state, as indicated by the disappearance of the greenish-yellow color. If an excess of stannous chloride has been originally added, it is of course unnecessary to add more. In any case, to avoid too great an excess of stannous chloride, which is undesirable it is advisable to add a few drops of potassium permanganate solution to the reduced mixture to once more slightly oxidize the solution. The solution, in its slightly oxidized condition, should be kept warm until ready to titrate and then the final reduction made with a drop or two of stannous chloride, avoiding unnecessary excess. Now wash down the sides of the beaker and add, while stirring, 5 cc. of the mercuric chloride solution to take up the excess of stannous chloride. Have ready a 500-cc. beaker containing 6–8 cc. of the manganese sulphate solution and about 400 cc. of cold water. Wash the iron solution into this and titrate at once with potassium permanganate in the usual way.

Ores containing organic matter, some magnetites, and pyritous ores require the usual precautions. With ores containing very large amounts of organic matter, it is generally most advantageous to burn off directly and follow the regular method. Ores containing small amounts of organic matter and slightly pyritous ores are dissolved in hydrochloric acid and oxidized with potassium chlorate, after which the regular method is pursued. Heavy sulphides may be treated with nitric acid as described in **29**, and the hydrochloric acid solution eventu-

ally obtained treated as above. Magnetites should be ground very fine in an agate mortar and then, if it is impossible to effect complete solution, either the ore or the insoluble residue may be treated as described in 17.

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[1] In regard to the functions of the manganese sulphate, read the Remark beginning on page 562 in Hall's translation of Treadwell's "Analytical Chemistry," Vol. II. (Wiley & Sons, N. Y.)

Some of the essential points in the Remark are as follows:

Dilute permanganate solution does not decompose cold dilute hydrochloric acid in the absence of ferrous iron. When ferrous iron is present, however, decomposition occurs, with a noticeable evolution of chlorine. In the presence of only a ferric salt, under similar conditions, there is no decomposition. These facts indicate that there is no direct action of the permanganate upon the hydrochloric acid, and that decomposition of the hydrochloric acid is due to the intermediate formation of a peroxide. (Fe_2O_5.)

The presence of considerable manganous salt prevents the decomposition that would otherwise occur. It does this by combining with the excess of oxygen in the intermediate peroxide, more quickly than the oxygen can attack the hydrochloric acid. MnO_2 is formed, which gives up 1 oxygen to ferrous iron to the end. When the oxidation of the ferrous iron is complete, no more MnO_2 will be formed.

If the concentration of the manganous salt is too low, the peroxide salt will decompose hydrochloric acid:

$$Fe_2O_5 + 10HCl \rightarrow 2FeCl_3 + 5H_2O + 2Cl.$$

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24. Dichromate Method.—The following solutions are required:

Stannous Chloride.—This should be strongly acid and should contain about 15 grams of tin, and 350 cc. of strong hydrochloric acid to the liter. It may be made by dissolving the tin in the acid by the aid of heat and diluting. It is usually more convenient to prepare it from the crystallized stannous chloride as follows: Dissolve 14.5 grams of the crystals in 165 cc. of strong hydrochloric acid and dilute to 500 cc. Keep in a half-liter bottle in which a stick of pure tin is placed to prevent oxidation. One cubic centimeter of this solution will reduce about 0.015 gram of iron from the ferric to the ferrous condition. It will naturally become somewhat stronger as the stick of tin gradually dissolves in the acid liquid.

Mercuric Chloride.—Use a saturated solution and keep an excess of the crystals in the bottle. Such a solution will contain at least 60 grams of mercuric chloride to the liter. About 1.2 cc. of this solution will oxidize the tin in 1 cc. of the above stannous chloride solution, at its original strength, to the stannic condition.

Potassium Ferricyanide.—This solution should be dilute, say 0.1 gram in 15 cc. of water. The exact strength is immaterial. It is best made frequently, or when required, in small quantity, as the solution does not keep indefinitely.

25. Standard Potassium Dichromate.—This should contain 4.39 grams of the pure salt per liter. On the basis of 0.5 gram of ore being taken for assay, 1 cc. of a solution of exactly this strength will equal 1 per cent of iron. This is shown by the equation

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl \rightarrow 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O.$$

Thus 1 molecule of potassium dichromate oxidizes 6 molecules of ferrous chloride to ferric chloride, or, 1 molecule of $K_2Cr_2O_7 = 6Fe$. This corresponds to 294.2 parts of $K_2Cr_2O_7$ to 335.04 parts of Fe. Hence 1 per cent, or 0.005 gram of iron when 0.5 gram of ore is taken for assay, requires 0.00439 gram of $K_2Cr_2O_7$. If this amount is contained in 1 cc. then the liter will contain 4.39 grams of $K_2Cr_2O_7$.

26. Standardize the dichromate solution as follows: Weigh carefully 0.15–0.20 gram of the purest iron wire obtainable (see remarks in 4 relative to the iron used for standardizing) and dissolve it in an 8-oz. flask in a mixture of 5 cc. each of strong nitric and hydrochloric acids. When the wire has dissolved add 5 cc. of strong sulphuric acid and boil over a free flame (manipulating the flask in a holder) until the hydrochloric and nitric acids are expelled and most of the sulphuric also. Before adding the sulphuric acid see that all salts are in solution (if necessary adding more hydrochloric acid), otherwise separated nitrates may not be completely decomposed. Allow to cool, add about 30 cc. of water and 5 cc. of strong hydrochloric acid and heat the mixture gently until solution is complete.

27. To the hot solution now add the stannous chloride solution cautiously until decolorization is complete, avoiding more than a slight excess. Transfer the reduced solution to a large beaker, washing out the flask with cold water. Add about 10 cc. of the mercuric chloride solution, pouring it in rapidly while stirring the mixture. If only a slight excess of stannous chloride was used, the 10 cc. of mercuric chloride will be ample and a white precipitate will be produced, but if the excess of stannous chloride was large the precipitate may become gray or black from the separation of metallic mercury. This discoloration should be watched for carefully, and if the faintest trace of it appears an abundance of the mercuric chloride solution should be

added at once. If this restores the pure white color the test may proceed; otherwise it is spoiled and must be begun anew.

The reactions involved are, first,

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4.$$

The stannous chloride thus reduces the ferric to ferrous chloride and becomes itself oxidized to stannic chloride. The excess of stannous chloride added, when treated with sufficient mercuric chloride, is oxidized to stannic chloride as follows:

$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2.$$

Mercurous chloride is produced, which is a white precipitate. If the excess of stannous chloride is large, however, so that the mercuric chloride added is insufficient for the last reaction, the following takes place:

$$SnCl_2 + HgCl_2 \rightarrow SnCl_4 + Hg.$$

The finely divided metallic mercury discolors the liquid. If more mercuric chloride be added at once, the mercury may frequently be taken into combination again:

$$Hg + HgCl_2 \rightarrow Hg_2Cl_2.$$

The liquid therefore contains, as a final result, ferrous chloride, stannic chloride, mercuric chloride, and a precipitate of white mercurous chloride. The only one of these compounds affected by the dichromate in the subsequent titration is the ferrous chloride.

28. The mixture in the beaker is now ready for the titration, which should proceed without delay, since after the mercuric chloride has been added there is nothing to prevent oxidation of the ferrous solution. Have ready a glazed porcelain tile either with or without depressions, a beaker or glass full of water in which is placed a glass rod, and also the test solution of potassium ferricyanide. Run in the dichromate solution from the burette while stirring the iron solution, and from time to time place a drop of the latter on the porcelain and touch it with a drop of the ferricyanide. For the latter purpose use the rod placed in the glass of water, and after each test return it to the glass; it will thus be kept sufficiently washed. As long as a large amount of iron still remains in the ferrous condition the ferricyanide will produce intensely blue tests. In order not to be deceived in the

matter, endeavor to add a sufficiently large drop of the ferricyanide each time to combine and produce a blue color with all the ferrous chloride present in the test drop. Continue to thus run in the dichromate solution until the color of the tests becomes fainter. Proceed then with more caution, finally drop by drop, until a test is obtained that fails to show a blue tint after half a minute. In making the final tests use less and less of the ferricyanide, as the delicacy of the reaction depends upon having just about enough ferricyanide present to combine with the ferrous chloride still remaining, an excess producing an abnormal color that obscures the true end-point. Finally read the number of cubic centimeters used, and, from the weight of iron taken, calculate the value of 1 cc. in iron.

Example.—Suppose 0.17 gram of iron wire, actually containing 0.1697 gram of iron, were taken, and that 33.8 cc. of dichromate solution were used. Then the value of 1 cc. is $0.1697 \div 33.8$, or 0.005021 gram of iron.

When 0.5 gram of ore is taken for assay, 1 cc. of the dichromate solution will equal 1.004 per cent of iron.

29. Treatment of an Ore.—Take 0.5 gram of the ore. The method of decomposition will depend upon the nature of the sample. Whenever possible, hydrochloric acid alone should be used. When the sample appears to be more or less of an oxidized nature always try hydrochloric acid first, using 10 cc. and warming the mixture in an 8-oz. flask. Take all the time and acid necessary, but do not boil violently, as this weakens the acid and fails to effect as rapid a solution as a gentler heat. If undecomposed sulphides remain, add 1–2 cc. of strong nitric acid and continue the heating. The final insoluble residue should be clean and white. If hydrochloric acid alone effects a complete decomposition, boil the solution finally to pastiness, add about 30 cc. of water and then 5 cc. of strong hydrochloric acid. These last operations are simply to insure about the proper proportion of acid present for the succeeding steps. If nitric acid has been used in the decomposition, first see that all soluble matter is still held in solution (otherwise adding more hydrochloric acid), then add 5 cc. of strong sulphuric acid and boil, preferably over a free flame, as nearly as possible to dryness, so as to expel most of the sulphuric acid. It is very difficult, if not impossible, to completely decompose solid nitrates that have separated from the solution by concentration, by boiling with sulphuric acid. After cooling, add about 75 cc. of water and

5 cc. of strong hydrochloric acid. It is unnecessary to heat the mixture to effect solution of the salts at this stage.

Observe that whatever method of decomposition is employed there is finally obtained a solution or mixture containing about 5 cc. of free hydrochloric acid.

30. To the mixture in the flask add about 0.2 gram of pure cupric sulphate and see that it dissolves, or better, an equivalent amount of strong solution. Now add about 20 grams of pure, finely granulated test-lead, and boil gently to effect the reduction of the iron to the ferrous condition. The copper precipitates on the lead and prevents it from cohering in lumps. If the ore already contains sufficient copper it is of course unnecessary to add more. Avoid adding the lead to a boiling-hot solution or it will probably produce a sudden evolution of steam and overflow the flask. The iron is usually entirely reduced by about five minutes' gentle boiling. It is best to boil for a few minutes after the liquid has become completely decolorized. The copper is thus all precipitated and any arsenic or antimony also removed from the solution. Prolonged boiling causes the formation of too much lead chloride, which separates out and renders the solution difficult to filter. Filter boiling-hot, bringing the excess of lead upon the filter, and wash thoroughly with hot water. Receive the filtrate in a large beaker in which 5 cc. of strong hydrochloric acid and 2 cc. of the prepared stannous chloride solution (**24**) have previously been placed. The acid is simply to insure sufficient acidity and the stannous chloride is to reduce any ferric chloride that may possibly be present and keep it reduced. Stir the mixture in the beaker after filtration. As it contains a little stannous chloride the ferrous chloride will not become oxidized by standing a short time at this stage.

31. The burette and other arrangements being ready (as described in **23**), add 10 cc. of mercuric chloride solution (**24**) to the liquid in the beaker and titrate as described for the standardization of the dichromate solution (**28**). From the number of cubic centimeters of dichromate solution used and the known value in iron of 1 cc., calculate the percentage of iron in the ore.

32. Silicates, Refractory Oxides, etc.—Decompose these substances as described either in **17, 18, 19** or **21,** so as to finally obtain the iron in hydrochloric acid solution containing about 5 cc. of the strong acid. Proceed with this solution as described in **30.**

33. Standard Methods for the Analysis of Iron.*—*Determination of Silicon.*—Weigh 1 gram of sample, add 30 cc. nitric acid (sp. gr. 1.13); then 5 cc. sulphuric acid (conc.). Evaporate on hot plate until all fumes are driven off. Take up in water and boil until all ferric sulphate is dissolved. Filter on an ashless filter, with or without suction pump, using a cone. Wash once with hot water, once with hydrochloric acid, and three or four times with hot water. Ignite, weigh, and evaporate with a few drops of sulphuric acid and 4 or 5 cc. of hydrofluoric acid. Ignite slowly and weigh. Multiply the difference in weight by 0.4693, which equals the per cent of silicon.

Determination of Sulphur.—Dissolve slowly a 3-gram sample of drillings in concentrated nitric acid in a platinum dish covered with an inverted watch-glass. After the iron is completely dissolved, add 2 grams of potassium nitrate, evaporate to dryness and ignite over an alcohol lamp at red heat. Add 50 cc. of a 1 per cent solution of sodium carbonate, boil for a few minutes, filter, using a little paper pulp in the filter if desired, and wash with a hot 1 per cent sodium carbonate solution. Acidify the filtrate with hydrochloric acid, evaporate to dryness, take up with 50 cc. of water and 2 cc. of concentrated hydrochloric acid, filter, wash, and after diluting the filtrate to about 100 cc., boil and precipitate with barium chloride. Filter, wash well with hot water, ignite and weigh as barium sulphate, which contains 13.71 per cent of sulphur.

Determination of Phosphorus.—Dissolve 2 grams sample in 50 cc. nitric acid (sp. gr. 1.13), add 10 cc. hydrochloric acid and evaporate to dryness. In case the sample contains a fairly high percentage of phosphorus it is better to use half the above quantities. Bake until free from acid, redissolving in 25 to 30 cc. of concentrated hydrochloric acid, dilute to about 60 cc., filter and wash. Evaporate to about 25 cc., add 20 cc. concentrated nitric acid, evaporate until a film begins to form, add 30 cc. of nitric acid (sp. gr. 1.20) and again evaporate until a film begins to form. Dilute to about 150 cc. with hot water and allow it to cool. When the solution is between 70° and 80° C., add 50 cc. of molybdate solution. Agitate the solution a few minutes, then filter on a tared Gooch crucible having a paper disk at the bottom. Wash three times with a 3 per cent nitric acid solution and twice with alcohol. Dry at 100° to 105° C., to constant weight. The weight

* 1907 Report of the Committee of the American Foundrymen's Association.

multiplied by 0.0163 equals the per cent of phosphorus in a 1 gram sample.

To make the molybdate solution add 100 grams molybdic acid to 250 cc. water, and to this add 150 cc. ammonia, then stir until all is dissolved and add 65 cc. nitric acid (sp. gr. 1.42). Make another solution by adding 400 cc. concentrated nitric acid to 1100 cc. water, and when the solutions are cool, pour the first slowly into the second with constant stirring and add a couple of drops of ammonium phosphate.

Determination of Manganese.—Dissolve 1.10 grams of drillings in 25 cc. nitric acid (sp. gr. 1.13), filter into an Erlenmeyer flask and wash with 30 cc. of the same acid. Then cool and add about 0.5 gram of sodium bismuthate until a permanent pink color forms. Heat until the color has disappeared, with or without the precipitation of manganese dioxide, and then add either sulphurous acid or a solution of ferrous sulphate until the solution is clear. Heat until all nitrous oxide fumes have been driven off, cool to about 15° C.; add an excess of sodium bismuthate—about 1 gram—and agitate for two or three minutes. Add 50 cc. water containing 30 cc. nitric acid to the liter, filter on an asbestos filter into an Erlenmeyer flask, and wash with 50 to 100 cc. of the nitric acid solution. Run in an excess of ferrous sulphate and titrate back with potassium permanganate solution of equal strength. Each cubic centimeter of N/10 ferrous sulphate used is equal to 0.10 per cent of manganese.

Determination of Total Carbon.—This determination requires considerable apparatus; therefore, in order to put as many obstacles as possible out of the way of its general adoption, in cases of dispute your committee has left optional several points which were felt to bring no chance of error into the method.

The train shall consist of a pre-heating furnace, containing copper oxide (Option No. 1) followed by caustic potash (sp. gr. 1.20), then calcium chloride, following which shall be the combustion furnace in which either a porcelain or platinum tube may be used (Option No. 2). The tube shall contain 4 or 5 inches of copper oxide between plugs of platinum gauze, the plug to the rear of the tube to be at about the point where the tube extends from the furnace. A roll of silver foil about 2 in. long shall be placed in the tube after the last plug of platinum gauze. The train after the combustion tube shall be anhydrous cupric sulphate, anhydrous cuprous chloride, calcium chloride, and

the absorption bulb of potassium hydrate (sp. gr. 1.27) with prolong filled with calcium chloride. A calcium chloride tube attached to the aspirator bottle shall be connected to the prolong.

In this method a single potash bulb shall be used, a second bulb, as sometimes used for a counterpoise, being more liable to introduce error than correct error in weight of the bulb in use, due to change of temperature or moisture in the atmosphere.

The operation shall be as follows: To 1 gram of well-mixed drillings add 100 cc. of potassium copper chloride solution and 7.5 cc. of hydrochloric acid (conc.). As soon as dissolved, as shown by the disappearance of all copper, filter on previously washed and ignited asbestos. Wash thoroughly the beaker in which the solution was made with 20 cc. of dilute hydrochloric acid (1 : 1), pour this on the filter and wash the carbon out of the beaker by means of a wash-bottle containing dilute hydrochloric acid (1 : 1) and then wash with warm water until all the acid is washed out of the filter. Dry the carbon at a temperature between 95° and 100° C.

Before the apparatus is used a blank shall be run and if the bulb does not gain in weight more than 0.5 mm., put the dried filter into the ignition tube and heat the pre-heating furnace and the part of the combustion furnace containing the copper oxide. After this is heated start the aspiration of oxygen or air at the rate of three bubbles per second, to show in the potash bulb. Continue slowly heating the combustion tube by turning on two burners at a time, and continue the combustion for thirty minutes if air is used; twenty minutes if oxygen is used. (The Shimer crucible is to be heated with a blast lamp for the same length of time.)

When the ignition is finished turn off the gas supply gradually so as to allow the combustion tube to cool off slowly and then shut off the oxygen supply and aspirate with air for ten minutes. Detach the potash bulb and prolong, close the ends with rubber caps and allow it to stand for five minutes, then weigh. The increase in weight multiplied by 0.27273 equals the percentage of carbon.

The potassium copper chloride shall be made by dissolving 1 lb. of the salt in 1 liter of water and filtering through an asbestos filter.

Option No. 1.—While a pre-heater is greatly to be desired, as only a small percentage of laboratories at present use them it was decided not to make the use of one essential to this method; subtraction of the

weight of the blank will, to a great extent, eliminate any error which might arise from not using a pre-heater.

Option No. 2.—The Shimer and similar crucibles are largely used as combustion furnaces, and for this reason it was decided to make optional the use of either the tube furnace or one of the standard crucibles. In case the crucible is used it shall be followed by a copper tube 3/16 in. inside diameter and 10 in. long, with its ends cooled by water jackets. In the center of the tube shall be placed a disk of platinum gauze, and for 3 or 4 in. in the side towards the crucible shall be silver foil and for the same distance on the other side shall be copper oxide. The ends shall be plugged with glass wool, and the tube heated with a fish-tail burner before the aspiration of air is started.

Graphite.—Dissolve 1 gram of sample in 35 cc. of nitric acid (sp. gr. 1.13), filter on asbestos, wash with hot water, then with potassium hydrate (sp. gr. 1.1), and finally with hot water. The graphite is then ignited as specified in the determination of total carbon.

CHAPTER XVI

LEAD

MANY methods have been proposed for the technical determination of lead in ores, etc. The following method, which is the result of much patient experiment, is in daily use in my laboratory. This and the permanganate method are my preferences.

1. **Chromate Method.**[1]—Prepare the following solutions:

Extraction Solution.—Make a cold saturated solution of commercial sodium acetate in distilled water and filter it. Mix 1 volume with $1\frac{1}{2}$ volumes of distilled water and add to the mixture 25 cc. of glacial acetic acid per liter. Used nearly boiling in a wash-bottle.

Hydrochloric Acid Mixture.—Make a cold saturated solution of table salt in distilled water and filter it. To 1 liter of the filtrate add 150 cc. of distilled water and 100 cc. of strong hydrochloric acid. Used cold in a wash-bottle.

Potassium Dichromate.—A cold saturated solution of the powdered commercial salt in distilled water. Filter, or allow to settle.

Starch Solution.—See COPPER, 3.

2. **Treatment of an Ore.**—Weigh 0.5 gram of the ore into an 8-oz. flask. It is usually best to begin the treatment with 20 cc. of strong hydrochloric acid and heat gently until all iron oxide, etc., is in solution. This will also decompose galena and expel the hydrogen sulphide. If sulphides remain that resist hydrochloric acid, add 5 cc. of strong nitric acid and continue the heating. Finally, if necessary, add 5–10 cc. more hydrochloric acid and again heat, to bring all the lead chloride into solution.

3. Decomposition and solution having been satisfactorily effected add 5 cc. of strong sulphuric acid and boil, finally, over a free flame, until the white fumes are coming off copiously. Cool, add about 30 cc.

of water and heat to boiling. Allow to stand, hot, until the anhydrous ferric sulphate usually present has dissolved. Now add 10 cc. of alcohol (either grain or wood) and then cool to room temperature, or cooler, and filter through a 9-cm. filter. (The alcohol is not absolutely essential except for the low percentages, say below 10 per cent lead.) Wash the precipitate with cold dilute (1–10) sulphuric acid at least four times. Give the flask a final rinse with cold water.

4. Now open the filter carefully and spread it in the funnel. Wash the precipitate from it into the flask again with a jet of hot water, using as little as possible. Have about 25 cc. of extraction solution in a small beaker. Drop the filter into this and heat to boiling. Stir the paper about in the hot liquid so as to shred it as much as possible. This is to dissolve every trace of lead sulphate still adhering to the filter. Moisten a small wad of absorbent cotton placed in the apex of the funnel and pour the mixture in the beaker through it into the flask, rinsing out the beaker with hot water. Now, continue to wash the cotton with hot water, but do not allow the filtrate to reach a greater volume than about 150 cc. When the liquid is heated at this stage any separated or undissolved lead sulphate (except as below) will go into solution.

5. The procedure described in 4 suffices in the great majority of cases, but when barium is present some of the lead sulphate may fail to dissolve; therefore, when barium is known to be present, or in case of doubt, proceed as follows: Without removing the filter, rinse the lead sulphate back into the flask with a jet of hot water, using as little as possible. Lift the fold of the filter to catch any deposit underneath. Add 10 cc. of hydrochloric acid to the mixture in the flask and then boil to pastiness, almost to dryness. Now add about 25 cc. of extraction solution and boil. Continue to add extraction solution, while boiling, until all the lead sulphate has dissolved, avoiding unnecessary excess. Filter through the last filter into an 8-oz. flask and wash with hot water until the filtrate has reached a volume of about 150 cc. It is a good plan to have a similar flask, with a mark on it for comparison, so as to always obtain, approximately, the right volume.

6. Having obtained a solution of the lead sulphate, by procedure 4 or 5, dilute, if necessary, to a volume of approximately 150 cc. with

hot water, and heat to boiling. Add to the boiling solution, preferably with a pipette, 10 cc. of the prepared potassium dichromate solution. Boil the mixture very gently for about seven minutes. This is necessary to ensure a fixed constitution for the lead chromate, which is not quite normal. Longer boiling does no harm. Now filter through an 11-cm. filter. Wash out the flask with hot water and then wash the filter and precipitate ten times with a hot dilute solution of sodium acetate (50 cc. of a cold saturated solution of the commercial salt diluted to 1 liter), using about 5–6 cc. each time. Now again place the clean flask under the funnel, and, with a jet of the cold hydrochloric acid mixture, stir up and dissolve the precipitate on the filter and continue washing with the same mixture until all the residue and every trace of color are removed from the filter. Use at least 50 cc. of the mixture in any case, in order that the subsequent reactions may have the proper conditions. Wash the filter finally with cold water, or at once dilute the filtrate until the flask is half full. Either one of two procedures is now to be followed, according to the amount of lead apparently present.

7. *With Not Over 20 Per Cent Lead.*—Add 2 cc. of a 50 per cent solution of potassium iodide, mix and titrate at once (to avoid possible loss of iodine by volatilization) with a standard sodium thiosulphate solution until the brown color becomes faint; then add sufficient starch solution to produce a strong blue color and finish the titration very slowly, finally drop by drop, until the solution becomes a clear pale green with no tinge of blue. The end-point is very sharp and care must be exercised or it may easily be passed. It is best to have a white surface under the flask.

8. *With Over 20 Per Cent Lead.*—Pour all but about 25 cc. of the liquid in the flask into a beaker. To the solution still remaining, add about 25 cc. of the hydrochloric acid mixture and 2 cc. of the above potassium iodide solution. Mix and titrate at once with the standard thiosulphate until the brown color has become faint. Now add a portion of the solution reserved in the beaker and again titrate to a faint brown color. Continue thus until the last of the reserved solution has been rinsed into the flask; then finish the titration as in 7. In pouring from the beaker it is best to use a glass rod, so as to avoid having to wash the lip each time and unnecessarily increasing the volume of liquid in the flask, otherwise the latter may become inconveniently full.

9. Standardize the thiosulphate solution on pure lead. The thiosulphate solution used in the iodide copper method and containing about 19.5 grams of the crystallized salt per liter is satisfactory for lead. Convert about 0.2 gram of pure lead foil to sulphate by boiling in an 8-oz. flask with 6 cc. of strong sulphuric acid. Cool, add 30 cc. of water and boil for a moment. Now add 10 cc. of alcohol and cool to room temperature under the tap. Filter off the lead sulphate, washing in the usual manner, and continue as described for ores (4). Titrate as described in **8**.

One cc. of the thiosulphate will be found to equal a little more than 0.005 gram of lead, or something over 1 per cent on the basis of 0.5 gram of ore taken for assay. The copper value of the thiosulphate, multiplied by 1.076, will give a close approximation to the lead value.

Notes.—The final solution is not a very good solvent for iodine, and therefore, if much is liberated at once, there is danger of loss by volatilization. To avoid this, the procedure described in **8** for the higher percentages of lead has been found the best.

The amount of potassium iodide prescribed is much more than theoretically required in any case, but it is never safe to use less, as the reactions are then liable to proceed too slowly.

Testing the completeness of the extraction is rarely necessary, as the solution of all the lead sulphate is usually easily seen.

Prepare only a wash-bottleful of the dilute sodium acetate wash at a time, as, unless the solution is heated frequently, a fungus growth develops that will clog the filter.

If the end-point be passed in titrating, it may be "brought back" with a dilute solution of potassium dichromate or permanganate, of which the comparative value need not be known. Simply run in from a burette a measured number of drops until the blue color returns; titrate once more and take reading. Now again run in the same number of drops of the correction solution as before and again finish the thiosulphate titration and read the burette. Subtract the difference between the two readings from the first one to obtain the true end-point for the lead.

If, in titrating by portions, as in **8**, the end-point be slightly passed with any of the portions, no appreciable error will be introduced if more of the reserved solution be quickly added, as the thiosulphate solution is decomposed only very slowly by the acid mixture.

The constitution of the lead chromate is a vital point. It depends

upon the various conditions of heat, acidity, etc. By operating as described, differences in constitution are minimized and a slightly acid chromate of practically constant composition is obtained. The normal chromate, under the conditions obtaining, is difficult to maintain as such.

Bismuth in small amount does not interfere. With several per cent present, some may remain as basic sulphate with the lead sulphate and produce high results. If bismuth is suspected it may be removed, just before the lead chromate is filtered, by adding about 2 grams of citric acid dissolved in a little hot water. Any bismuth chromate will go into solution at once. Filter without delay.

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[1] In this method the lead is eventually precipitated as chromate, $PbCrO_4$. This is then decomposed by hydrochloric acid, as follows:

$$PbCrO_4 + 2HCl \rightarrow PbCl_2 + CrO_3 + H_2O.$$

Potassium iodide is now added, which the chromic acid decomposes with the liberation of iodine, according to the reaction,

$$CrO_3 + 6HCl + 3KI \rightarrow CrCl_3 + 3KCl + 3H_2O + I_3.$$

The iodine is titrated with thiosulphate.

The above reactions show that $Pb = CrO_3$, and, as $CrO_3 = I_3$, then $Pb = I_3$. In the titration, the reaction between the thiosulphate and iodine is,

$$2(Na_2S_2O_3) + I_2 \rightarrow 2NaI = Na_2S_4O_6.$$

The latter salt is sodium tetrathioanate. This reaction shows that $Na_2S_2O_3 = I$; therefore, $3(Na_2S_2O_3) = Pb$.

The formula of the crystallized thiosulphate is $Na_2S_2O_3 + 5H_2O$, and its molecular weight is 248.2. Accordingly, 3(248.2) parts by weight of the crystallized salt = 207.2 parts of Pb. As 0.005 gram = 1 per cent of Pb, we have the proportion,

$$744.6 : 207.2 = x : 0.005. \quad x = 0.01797.$$

This is the weight of the thiosulphate, in grams, to be contained in 1 cc., to be equal to 1 per cent of Pb. This gives 17.97 grams per liter. This theoretical strength does not apply in the actual analysis. With a known amount of pure lead it would appear slightly weak. As there are inevitable losses of lead in the process, due to the slight solubility of the sulphate and chromate, the solution should appear slightly strong, rather than weak. The explanation is that the lead chromate precipitate is not the normal $PbCrO_4$, but a slightly acid chromate. The slight excess of chromic acid more than counterbalances any loss of lead. More thiosulphate is required than would appear necessary, and therefore a solution based on the assumption that the $PbCrO_4$ is normal would appear weak.

An approximately correct solution, standardized empirically, is all that is

necessary. If the thiosulphate solution used for copper determinations is at hand, it may be employed. Once the operator, according to his personal manipulation, has established the relation between copper and lead in the thiosulphate titration, no further standardizing against lead is necessary. Simply standardize for copper by the permanganate method (see COPPER, **4**) and multiply by the proper factor as determined. This factor may vary slightly with different operators.

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10. Permanganate Method.*—This is a very satisfactory method in the absence of large amounts of calcium. As much as 10 per cent of CaO, however, does not interfere, as this amount of CaO, as sulphate, is soluble in the 100 cc. of acid liquid from which the lead sulphate is filtered. Larger amounts of CaO could undoubtedly be provided for by still greater dilution at this point, without serious effect in dissolving lead sulphate. Barium sulphate is not greatly affected by the chemical transformations, and what goes through to the end is sufficiently soluble, as oxalate, to remain in solution. At the outset, however, barium and lead form more or less of a double sulphate, in which the lead fails to be completely converted to carbonate. This would produce low results, were it not for the hydrochloric acid treatment of the sulphates, described below, which breaks up the compound.

11. Procedure.—Decompose 0.5 gram of the ore in an 8-oz. flask as described in 2. Decomposition having been effected, add 6 cc. of sulphuric acid and boil to strong fumes. Allow to cool, add 100 cc. of cold water and heat to boiling. Remove from the heat, add 10 cc. of alcohol (grain or wood), cautiously, and cool under the tap. Fold a 9-cm. filter, taking particular care to crease the fold that will come next to the precipitate as thin as possible, so it will lie flat and not easily allow material to get under the edge. Filter the cold mixture through this, returning the first portions of the filtrate if not clear. Wash six times with cold water containing 10 per cent of alcohol. Any traces of lead sulphate remaining in the flask will be recovered subsequently.

12. With a jet of hot water, using as little as possible, rinse the precipitate from the filter, through a short funnel, back into the flask. (In the known or assumed presence of barium, interpolate the following short procedure: Add 10 cc. of strong hydrochloric acid and boil over a free flame nearly to dryness. Allow to cool, add 20 cc. of water and a

* A. H. Low., Jour. Am. Chem. Soc., XV, 550. Modified.

few drops of ammonia, sufficient to neutralize the acid.) Place the flask again under the original funnel and pour through the filter 10 cc. of a cold saturated solution of ammonium carbonate. Remove the flask and heat the contents just to boiling, then cool completely under the tap. Pour the cold mixture through the original filter. The filtrate is to be rejected. Wash out the flask well with cold water, pouring through the filter, and then wash filter and precipitate ten times with cold water containing about 5 per cent of the ammonium carbonate solution.

13. Again using a jet of hot water, wash the precipitate from the filter into a small beaker. Add 5–6 cc. of glacial acetic acid and two or three drops of ammonia and heat to boiling. Replace the flask under the funnel and pour the hot acid mixture through the filter. Wash out the beaker with hot water and then wash the filter ten times with hot water slightly acidulated with acetic acid. (Small amounts of lead carbonate may be dissolved directly upon the filter without previous transference to a beaker.)

14. Add to the filtrate 10 cc. of a cold saturated solution of oxalic acid, heat to boiling and then cool completely, under the tap. Be particular to get as cold as possible. Now filter the lead oxalate through a 9-cm. filter. Using cold water, wash out the flask thoroughly and then wash filter and precipitate ten times.

15. Place about 25 cc. of cold water in the flask, add 5–6 cc. of sulphuric acid and then about 100 cc. of hot water. Drop in the filter and precipitate. Wipe out any lead oxalate adhering in the funnel with a small piece of filter-paper and drop into the flask. Heat the acid mixture nearly to boiling and then titrate it with standard potassium permanganate solution to a faint pink tinge. Calculate the result from the known lead value of the permanganate.

16. The permanganate used for iron titrations will serve, although rather strong for lead. Theoretically, 1.857 times the Fe factor will give the Pb factor. Owing to slight losses of lead in the process an empirical factor must be used. This is 1.861 times the Fe factor. Based on this factor and on 0.5 gram of ore taken for assay, 1 cc. of a permanganate solution containing 1.524 grams per liter will equal 1 per cent lead.

17. The permanganate may be standardized directly on lead as follows: Convert about 0.250 gram of pure lead-foil to sulphate by boiling with 6 cc. of sulphuric acid. Continue according to the entire

above process. Finally, divide the percentage value of the lead taken by the cubic centimeters of permanganate required, to obtain the percentage value of 1 cc. in lead. A comparison of this figure with the Fe value of the permanganate may be made, to check the conversion factor given above. The personal equation may make a slight difference.[1]

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[1] In this method the lead is first separated as sulphate, the sulphate is converted to carbonate and then the latter is dissolved in acetic acid, from which solution the lead is precipitated as oxalate. The separated oxalate is decomposed by sulphuric acid, setting free oxalic acid which is then titrated with permanganate. Thus the oxalic acid determined is a measure of the lead with which it was combined.

The formula for lead oxalate is PbO_4C_2. The reaction with sulphuric acid is, $PbO_4C_2+H_2SO_4 \rightarrow PbSO_4+H_2O_4C_2$. Every molecule, then, of oxalic acid set free is equivalent to 1 Pb.

In the titration, the oxalic acid is oxidized to carbon dioxide and water, as follows: $H_2O_4C_2+O \rightarrow 2CO_2+H_2O$. This shows that every $H_2O_4C_2$ requires one O, or, $=O$. As $H_2O_4C_2$ is equivalent to Pb, then $Pb=O$.

When ferrous iron is oxidized by permanganate, FeO is changed to Fe_2O_3, as follows: $2FeO$, or, $Fe_2O_2, +O=Fe_2O_3$. This shows than $Fe_2=O$. As $Pb=O$, then $Fe_2=Pb$. That is, 111.68 parts by weight of $Fe=207.2$ parts of Pb, or, 1 part of $Fe=1.857$ parts of Pb. This is the theoretical factor for converting the Fe value of 1 cc. of the permanganate to the Pb value.

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18. Alexander's Method, Modified.—Alexander's method, or some modification of it, is the one most commonly employed in western smelting works. The principal objections to it that I have noted are the difficulty of accurately determining very low percentages of lead, on account of the slowness of the reactions in such cases, and the occasional failure to obtain checking results or satisfactory end-points with the higher percentages, for no apparent reason. The following modification was long used in my laboratory.

Treat 0.5 gram of the ore precisely as described in 2 and 3 and extract the lead sulphate as described in 4. Add to the filtrate in the flask an excess of ammonium sulphide. It is a good plan, although not essential, to first add a little ammonia to neutralize the acid and prevent separation of sulphur. Boil for a moment to coagulate the lead sulphide and then filter and wash with hot water. These operations entirely remove any calcium sulphate.

19. The lead sulphide is still almost certain to contain a little iron. This iron is originally retained by the lead sulphate. If allowed to remain it tends to obscure the end-point of the subsequent titration by producing a color with the tannic acid used for testing. It is best, therefore, to remove any possible iron in every case as follows: pour through the precipitate on the filter a mixture of 5 cc. of the dilute (1 : 1) sulphuric acid and 15 cc. of strong hydrogen sulphide water, and then wash with cold water.

20. Now drop filter and contents into the flask and add 5 cc. of strong hydrochloric acid. Boil the mixture, best by manipulating the flask over a small free flame to prevent bumping, to convert the lead to chloride and expel hydrogen sulphide, the filter meanwhile becoming well disintegrated. If 5 cc. of acid prove insufficient to entirely decompose the lead sulphide, add a little more, but avoid using a large excess. In any case, boil off half or more of the acid and then, to the hot mixture, add 2–3 drops of strong nitric acid to oxidize any unexpelled hydrogen sulphide. Now add 25 cc. of cold water, then a few drops of litmus solution as an indicator, and then cautiously add ammonia in very slight excess. Finally, make distinctly acid with acetic acid.

21. Heat the mixture in the flask to boiling, dilute to about 200 cc. with boiling-hot water, and titrate with the standard ammonium molybdate solution as follows: Pour about two-thirds of the hot lead solution into a large beaker and run the molybdate solution into it from a burette until a drop from the beaker, when placed on a glazed porcelain plate and touched with a drop of a solution of tannic acid (about 0.1 gram dissolved in 20 cc. of water), gives a brown or yellow tinge. Now add more of the lead solution from the flask and continue the titration until the end-point is again passed. Continue thus to approach the true end-point, using more caution each time. Finally, when only a few cubic centimeters remain in the flask, pour the entire mixture in the beaker into the flask and then back into the beaker again and finish the titration 2 drops at a time. When the final yellow tinge is obtained, some of the immediately preceding tests may have developed a tinge also. From the reading of the burette deduct the volume of 2 drops for each test thus showing a color. Multiply the corrected reading by the percentage value of 1 cc. of the molybdate solution in lead to obtain the percentage of lead in the ore.

22. Standard Molybdate Solution.—This should contain about 4.26 grams of ammonium molybdate per liter, in order that when 0.5 gram of ore is taken for assay 1 cc. shall equal about 1 per cent of lead.

Standardize as follows: Weigh carefully about 0.2 gram of pure lead foil and dissolve in an 8-oz. flask by warming with a mixture of 2 cc. of strong nitric acid and 4 cc. of water. When dissolved, boil nearly or quite to dryness, add about 30 cc. of water, and see that all the lead nitrate dissolves. Now add 5 cc. of strong sulphuric acid, boil the mixture a moment, cool to room temperature, and allow to stand and settle a short time. Filter and wash with dilute (1 : 10) sulphuric acid. Proceed with the filtered lead sulphate precisely as described for the assay of an ore (in **18** et seq.), except that the purification of the lead sulphide described in **19** may be omitted. I formerly dissolved the lead sulphate directly in a hot solution of ammonium chloride and acetate and titrated at once. It was observed, however, that the large amount of ammonium salts necessary to effect complete solution of the lead sulphate hindered the separation of lead as molybdate during the titration, and the end-point was not as sharp as that obtained by the method described.

Divide the weight of lead taken by the number of cubic centimeters of molybdate solution used. This will give the weight of lead corresponding to 1 cc. of molybdate. From this figure calculate the percentage value of 1 cc. on the basis of 0.5 gram of ore taken for assay. One cc. of the molybdate solution should thus equal about 0.005 gram of lead, or about 1 per cent.

23. Shorter Method for Ores containing Little or No Calcium.—Alexander's original method did not sufficiently provide for the presence of calcium, which is a frequent constituent of lead ores. It was partially to avoid this source of error that the method was modified as above. Calcium forms a molybdate which is more or less insoluble under the conditions of the titration and tends to raise the results in a rather irregular manner. When it is known to be absent or present only in small amount (as may frequently be noted from the appearance of the lead sulphate on the filter), the above process may be shortened as follows:

24. Begin as usual and proceed until the washed lead sulphate precipitate is obtained on the filter. Place the precipitate and filter in the original flask, add 10 cc. of strong hydrochloric acid and boil until the filter is well disintegrated, then add 15 cc. of strong hydro-

chloric acid, 25 cc. of cold water and 25 cc. of strong ammonia water. Now color with a little litmus solution, make slightly alkaline with ammonia if not already so, and then make distinctly acid with strong acetic acid. Heat to boiling and see that the lead sulphate is entirely dissolved, then dilute to about 200 cc. with boiling-hot water and titrate as previously described (21).

25. Even in the absence of calcium this method is liable to be unsatisfactory. The lead sulphate precipitate will frequently retain iron that cannot be dissolved or washed out, but which finally goes into solution with the lead sulphate and gives a color with tannic acid on the test-plate. The large amount of salts present also obscures the end-point and hinders the precipitation of the lead molybdate. This is especially noticeable with very low-grade ores. Except, therefore, for hasty approximate results, it is generally best to use the somewhat longer method first given.

26. **Ferrocyanide Method.***—This method gives very good results and is preferred by some chemists.

It is better to start with 1 gram, rather than 0.5 gram of the ore. Decompose in an 8-oz. flask precisely as described for the chromate method (2). Continue as there directed until the washed mixture of lead sulphate and gangue is obtained on the filter. The last two washings should be with pure water, to remove most of the acid. See that the filter is well creased, so as to lie as flat as possible and prevent solid matter from getting under the fold. Place a funnel in the original flask (which should be free from acid) and rinse the contents of the filter (without removing it from its funnel) into it as completely as possible with cold water. Not more than 50 cc. of water need be used. Add 10 cc. of a cold saturated solution of commercial ammonium carbonate, pouring it through the original filter, and heat the mixture to boiling. The heating is necessary to ensure the complete conversion of any possible calcium sulphate to carbonate. Cool to ordinary temperature, under the tap or otherwise, and filter through the original filter, washing flask and precipitate thoroughly with cold water. Place in the flask some dilute acetic acid, equivalent to a mixture of about 5 cc. of the glacial acid and 25 cc. of water, and have it heating while the filter is being washed. The flask usually contains a small residue of lead carbonate which is thus recovered. Place the filter and contents in a large beaker and add the boiling hot

* A. H. Low., Jour. Am. Chem. Soc., XV, p. 550.

acetic acid. Stir the mixture about until the carbonates are entirely dissolved, heating if necessary. Dilute with about 100 cc. of cold water and the solution is ready for titration with standard potassium ferrocyanide solution. The end-point is indicated by the usual brown tinge when a drop is tested on a porcelain plate with a drop of a saturated solution of uranium acetate. Reserve a portion of the solution and titrate the main body rapidly until the end-point is passed; then add most of the reserved portion and titrate with more caution until the end-point is once more passed. Finally rinse in the balance of the reserve and finish the titration 2 drops at a time, stirring well after each addition. When the final brown tinge is thus obtained, allow a little time for the immediately previous tests to develop and then deduct from the burette reading an amount equal to 2 more drops than are indicated by the tests, as a solution containing no lead shows the test only after the addition of the third drop of ferrocyanide.

27. The standard ferrocyanide should contain about 10 grams of the crystallized salt to the liter.[1] On the basis of 1 gram of ore taken for assay, 1 cc. of this solution will equal about 1 per cent lead. It is standardized on 0.3 to 0.4 gram of pure lead, reduced from the acetate. This is converted to sulphate by boiling with about 7 cc. of strong sulphuric acid, and put through the entire process.

28. While the above method answers in ordinary cases, in order to provide against bismuth and antimony (the basic sulphates of which might cause trouble), the following modification may be adopted: To the sufficiently cool residue of the sulphuric acid evaporation add 10 cc. of dilute sulphuric acid (1 : 10) and about 2 grams of Rochelle salt. When this has dissolved, add 40 cc. of water, heat to boiling and proceed as usual.

Calcium does not interfere with this method except by the slight solvent action exercised by calcium acetate on the brown uranium acetate of the test. Thirty per cent of CaO in an ore, however, occasions no serious trouble. Calcium sulphate must not be allowed in the acetate solution, as it might occasion a loss of lead by precipitation as sulphate.

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[1] One molecule of potassium ferrocyanide, $K_4Fe(CN)_6$, precipitates 2 atoms of Pb as ferrocyanide, $Pb_2Fe(CN)_6$. The crystallized potassium ferrocyanide has the formula $K_4Fe(CN)_6+3H_2O$ and its molecular weight is 422.366. This is equal to 2Pb, or 414.4 parts by weight. This makes 1 per cent Pb, or, 0.01 gram, =0.01019

gram of ferrocyanide, the amount to be contained in 1 cc. to equal 1 per cent Pb, or, 10.19 grams per liter.

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29. Decomposition of Refractory Material.—Metallurgical products, such as antimonial slags, may obstinately resist the ordinary methods of attack. In such cases try the following plans, First *A*, and then, if that fails, try *B*. The latter is more troublesome but will probably succeed in almost any case.

A. Treat 0.5 gram of the finely ground material precisely as described in ANTIMONY, 2. With oxidized material the piece of filter paper is very essential. It causes a reduction of antimony to the *ous* condition and thus promotes its solution. In the presence of much sulphur or carbon the paper is unnecessary. To the cool melt add 5 cc. of sulphuric acid, 10 cc. of water and 5 cc. of hydrochloric acid. Boil to strong fumes. Cool, add 30 cc. of water, heat to boiling and then maintain hot, but not boiling, with occasional agitation, until the soluble salts, including any anhydrous ferric sulphate, are all dissolved. Add 10 cc. of alcohol, cool under the tap, filter and wash the lead sulphate as usual and proceed with it according to the method selected. If the permanganate method is to be employed, dilute with 100 cc. of water instead of 30.

B. Employ the peroxide fusion, as described for chrome iron ore (CHROMIUM, 2, 3). If sulphides or carbon are present, modify the method by the addition of sodium carbonate to prevent too violent action, as described in MOLYBDENUM, 1. In either case proceed to the point where the crucible has been removed from the solution of the melt. Cover the casserole and boil to a bulk of 100 cc. or less. Now transfer the mixture to an 8-oz. flask, retaining any scales of iron oxide in the casserole, cleansing them by several slight additions of water and decanting. Cool the mixture in the flask, acidify slightly with sulphuric acid (avoiding loss by effervescence) and then add 5 cc. in excess and 10 cc. of alcohol. Cool under the tap, filter off the lead sulphate and treat it as usual.

30. Determination of Lead in Fire Assay Button.—Hammer or roll the button out thin and weigh 0.250 gram. Transfer to an 8-oz. flask and convert to sulphate by boiling with 6 cc. of sulphuric acid. Cool, dilute with 30 cc. of water and continue as with an ore.

CHAPTER XVI.

MAGNESIUM

1. Method for Ores, etc.—Treat 0.5 gram of the ore in an 8-oz. flask with 10 cc. of strong hydrochloric acid, heating gently, avoiding boiling, to dissolve oxides, etc. Then, if sulphides are also present, add 5 cc. of strong nitric acid and continue the gentle heating until they are decomposed. Now boil to dryness to expel the acids (and render any separated silica insoluble). Warm the residue with 25 cc. of water and 1 or 2 cc. of strong hydrochloric acid, to effect solution of the salts, then transfer to a beaker, dilute to about 150 cc. with cold water and pass in hydrogen sulphide gas to remove copper, lead, etc. Filter, washing with dilute hydrogen sulphide water, and receive the filtrate in a large casserole ($5\frac{1}{4}$ in.). Now add 5 cc. of strong hydrochloric acid (to provide for the formation of sufficient ammonium chloride to prevent the subsequent precipitation of alkaline earths as carbonates), then 15–20 cc. of strong bromine water to oxidize the iron and remove manganese, and finally make alkaline with ammonia. Boil for a few moments, allow to settle somewhat, and then filter, washing with hot water. Reserve the filtrate. Continue from this point as described for calcium in CALCIUM, 2 and 3, until the filtrate from the calcium oxalate is obtained, or the combined filtrates, if two precipitations were made.

2. In my own laboratory, for ordinary technical work, especially when the amount of magnesium is supposed to be small, this filtrate is concentrated considerably by boiling in a large porcelain casserole and the magnesium is then precipitated by Handy's method (10). The precipitated magnesium ammonium phosphate is then ignited and weighed as $Mg_2P_2O_7$, as described in 4.

For more exact results proceed as follows:

3. Concentrate the filtrate from the calcium oxalate to small bulk by boiling in a large porcelain casserole, and when salts show a tendency

to separate, transfer to a platinum dish or smaller porcelain casserole, in separate small portions if necessary, and evaporate on the water-bath to complete dryness. When dry, ignite gently to expel the ammonium salts. Cool, dissolve the residue in a very little dilute hydrochloric acid, make very faintly alkaline with ammonia and filter if necessary. The magnesium is now precipitated by the method of W. Gibbs.*† (Or, proceed to 10 and finish with the precipitate as in 4, below.)

4. Heat the solution to boiling and add, drop by drop, a solution of sodium ammonium phosphate ($NaNH_4HPO_4.2H_2O$), 160 grams to the liter,‡ until no further precipitate is produced. Most of the magnesium is at once precipitated as amorphous, dimagnesium phosphate ($MgHPO_4$). Allow the solution to cool, and then, stirring constantly, add about one-third its volume of ammonia. By this procedure the precipitate is changed to crystalline magnesium ammonium phosphate ($MgNH_4PO_4$) and the magnesium remaining in solution is precipitated in the same form. Let the cold mixture stand two or three hours, and then decant the supernatant solution through a filter. Wash the precipitate three times by decantation with $2\frac{1}{2}$ per cent ammonia and then transfer to the filter and wash thoroughly with $2\frac{1}{2}$ per cent ammonia. Dry the filter and precipitate, transfer the latter as completely as possible to a weighed platinum crucible, burn the filter-paper in a platinum spiral and add the ash to the precipitate in the crucible. Cover the crucible and heat it, gently at first to expel the ammonia, and then over the blast-lamp until the residue is pure white. Cool in desiccator and weigh as $Mg_2P_2O_7$. This weight, multiplied by 0.2184 will give that of the Mg, or, if multiplied by 0.3620, that of the MgO.

5. In the above method it is not usually considered necessary to remove, as sulphide, any zinc present, inasmuch as the ignition to expel ammonium salts will tend to drive off the zinc as chloride. Should a little still remain, it is not likely to precipitate as phosphate on account of the presence of the ammonia and ammonium salts added.

6. Note on the Precipitation of Magnesium Ammonium Phosphate.—If the precipitation is made in a strongly ammoniacal solution instead of as described, some tribasic magnesium phosphate ($Mg_3P_2O_8$)

* Am. Jour. Sci., (3) 5, 114.

† I usually prefer to precipitate by Handy's method, finally weighing the pyrophosphate, however, as described by Gibbs.

‡ 27 cc. of this solution will precipitate 0.5 gram of magnesium.

will almost invariably form. This will be unchanged by the ignition and cause low results. It is, therefore, necessary to add the excess of ammonia later, but even in this case, if ammonium salts are present, the precipitate will always contain monomagnesium ammonium phosphate ($Mg(NH_4)_4(PO_4)_2$), which requires intense heating to constant weight to be certain it has all changed to $Mg_2P_2O_7$.

7. H. Neubauer,* whose experiments demonstrated the above facts, proceeds as follows: Slightly acidify the filtrate from the calcium oxalate with hydrochloric acid and then add an excess of sodium phosphate solution and one-third the solution's volume of 10 per cent ammonia, stirring constantly. Allow to stand twenty-four hours and then wash by decantation, through a filter, with a little $2\frac{1}{2}$ per cent ammonia. It is better to evaporate the filtrate from the calcium oxalate to dryness and expel the ammonium salts by ignition, as previously described (3). If this is done, the solution may be filtered after only four hours' standing instead of twenty-four. Place the beaker containing most of the precipitate under the funnel and pour through the filter a little dilute hydrochloric acid, washing the filter with hot water. Enough acid should be used to effect the solution of the precipitate in the beaker. Add now some ammonium chloride, a few drops of sodium phosphate solution, and one-third of the solution's volume of 10 per cent ammonia. Allow to stand four hours. Pour the solution through a filter, wash the precipitate three times by decantation with $2\frac{1}{2}$ per cent ammonia, then transfer it to the filter and wash it thoroughly with the dilute ammonia. Dry and ignite the precipitate as previously described (4).

8. **Limestones, Silicates, etc.**—In material of these classes the members of the hydrogen sulphide group are usually absent, and, accordingly, no steps are necessary to remove them. When the substance is decomposable by acids the procedure is, with this exception, the same as previously described for ores (1). The treatment of silicates is begun as described for calcium on similar material (CALCIUM, 7), but inasmuch as the magnesium is to be determined gravimetrically it is necessary to evaporate the acid solution to dryness, and remove the silica with the usual precautions (SILICA, 10). The acid solution, free from silica, is then treated as described for ores, usually omitting the hydrogen sulphide treatment.

* Zeit. f. angew. Chem., 1896, 439. Treadwell, Quant. Anal., Hall, 2d Ed., p. 65.

9. Handy's Volumetric Method.*—This is a modification of Stolba's method in which the precipitated magnesium ammonium phosphate is titrated with standard sulphuric acid, the reaction being

$$MgNH_4PO_4 + H_2SO_4 \rightarrow MgSO_4 + NH_4H_2PO_4.$$

A measured excess of sulphuric acid is used and titrated back with standard sodium hydroxide. The results obtained are very satisfactory.

The ore or other material is treated by the usual methods and the filtrate from the calcium oxalate precipitation is then treated as follows:

10. Add ammonia (sp. gr. 0.90) equivalent to 1/10 of the solution. Cool in water to 20° to 25° C. Precipitate by adding slowly with constant stirring a saturated solution of sodium ammonium phosphate, using 1 cc. for each 0.01 gram magnesium oxide. Stir vigorously for five minutes or shake in a flask for an equal length of time. In the former case let the solution stand until the clarification of the upper liquid shows that the reaction is complete. In the case of flask precipitations, if over 0.002 gram of magnesium oxide is present the solution may be filtered in fifteen minutes. Suction may be used if desired, but if many solutions are to be filtered at once little is gained by its use. Use 10 per cent ammonia wash (1 part ammonia (sp.gr. 0.90) to 9 of water). Deliver it preferably from an aspirator bottle placed about 4 ft. above the bench. Wash by decantation as far as possible. Finally, wash the precipitate which has gone on the filter back into the beaker, stir it up with the ammonia wash and bring it again completely on the filter-paper. Wash once more, leaving the upper edge of the filter clear of precipitate so that it can be handled. Avoid assembling all of the precipitate in the apex, but leave it fairly evenly distributed over the lower two-thirds of the paper. Allow the precipitates to drain and then transfer each in turn to a dry 5-inch filter-paper, allowing them to remain there, open and face upward, until the bulk of the moisture has been absorbed. After about three minutes transfer them to fresh dry filters, and in the case of heavy precipitates to a third set a few minutes later. Then place the filters on a shelf to dry at the temperature of the room, or place filter papers and backing on the grating of an air oven having a temperature of 50° to 60° C. After fifteen or twenty minutes in the oven, or forty-five minutes in the air, watch for the time when the filters have dried

* James Otis Handy, Jour. Am. Chem. Soc., XXII, p. 31.

inward half an inch from the margin. This appearance has been found to indicate that the evaporation has gone far enough to insure the expulsion of the free ammonia. Now place the precipitates and filters in small dry beakers and treat each with a measured excess of decinormal sulphuric acid, stirring until the papers are disintegrated and the precipitates dissolved. Then add 2 drops of a 0.1 per cent alcoholic solution of methyl orange. If this gives a clear decided pink, enough acid has been added. If it is only faintly pink, the excess of acid is slight and some minute particles may have escaped solution. In such cases add 5 cc. more decinormal sulphuric acid and stir well. Finally, dilute to about 100 cc. and titrate back with decinormal sodium hydroxide solution to the appearance of a clear yellow color, free from all suggestion of pink.

1 cc.N/10 H_2SO_4 = 0.002 gram MgO.*

If the filtrations have taken place during the latter part of the day, the filters may be removed from the funnels and allowed to stand overnight, after which they are titrated as described.

11. **Notes on the above Method (Handy).**—If the drying of the precipitate proceeds too far, solution in decinormal sulphuric acid is slow. If, however, the drying is stopped at the point described, there is enough moisture left so that, on stirring, the precipitate blends quickly with the acid and soon dissolves.

The tendency of magnesium to precipitate with iron and aluminum and with calcium oxalate must be met by re-solution in hydrochloric acid and reprecipitation. When the amount of calcium is considerable it is best to burn off the first oxalate precipitate before dissolving in hydrochloric acid. By this means the oxalate is decomposed and the addition of ammonia alone does not cause its sudden reprecipitation. Even in the second precipitation, if the boiling is allowed to proceed longer than is necessary to make the finely crystalline calcium oxalate settle well, some magnesium oxalate is sure to precipitate, betraying its presence by its coarser texture. The solution for magnesium precipitation usually does and always should contain in the form of ammonium chloride the equivalent of 5 cc. of concentrated hydrochloric acid per 100 cc.

* More accurately, 0.002016 gram MgO. 1 cc. N/10 H_2SO_4 = 0.0049038 gram H_2SO_4. The reaction (9) gives the proportion 98.076 : 40.32 = 0.0049038 : x. x = 0.002016.

CHAPTER XVIII

MANGANESE

1. THE following methods for the determination of manganese are applicable to most ores, the first one being ordinarily employed in my own laboratory. In unusual cases, where the material fails to be sufficiently decomposed by simple acid treatment, the mode of attack calls for the exercise of the operator's judgment. It is usual in such cases to employ one of the methods described under IRON (17, 18, et seq.), and eventually to bring the solution of the substance into a proper condition for continuing by the regular method.

2. **Usual Method for Ores, etc.**[1]—Treat 0.5 gram of the substance in an 8-oz. flask with whatever acids are necessary to decompose it. For an oxidized ore, about 10 cc. of strong hydrochloric acid are usually sufficient. With mixed ores it is best, in most cases, to start with hydrochloric acid, to dissolve the oxides, and then add 5–10 cc. of strong nitric acid to decompose the sulphides. With pure, or nearly pure, sulphides, begin at once with 10 cc. of nitric acid.

3. Heat very gently at first until the decomposition is complete. Finally add about 5 cc. of strong sulphuric acid and heat strongly, best over a free flame, almost to dryness. Cool and add about 100 cc. of water. Boil the mixture a moment and allow to stand, hot, with occasional shaking, until anhydrous ferric sulphate, etc., has dissolved (a minute or two). Add 1 or 2 grams of finely powdered (not lumpy) zinc oxide and heat to boiling. Remove from the heat and continue to add zinc oxide in small portions, while shaking, until all iron is precipitated and a moderate amount of white zinc oxide remains in the bottom of the flask.* Be sure that the iron is all down. Heat to boiling (liable to foam) and then filter through an 11-cm. filter having a small wad of wetted absorbent cotton in the apex. Wash ten times with hot water, receiving the filtrate in a 500-cc. beaker. If any lead is likely to be present, add 2 cc. of a saturated potassium dichromate solution before the final boiling.[2]

4. Add to the filtrate 3–4 grams of sodium acetate, or about 5 cc.

* As long as the zinc oxide is precipitating iron it becomes colored brown with ferric hydroxide; as soon as an excess remains *white* it indicates that all the iron has been precipitated.

of a saturated solution, and 30 cc. of saturated bromine water.* Heat to boiling and boil several minutes.[3] If bromine vapors do not appear above the liquid in the covered beaker, add more bromine water until they do. This shows the necessary excess.

5. Filter through an 11-cm. filter and wash ten times with hot water. Any MnO_2 adhering in the beaker is simply washed clean and left there. It will be recovered later. The filtrate should be clear. If desired, it may be further tested by boiling with more bromine water.

6. Place the washed precipitate, together with the filter, back in the beaker and run in from a burette what is judged to be an excess of the standard oxalic acid solution, described below (9). On the basis of 0.5 gram of ore taken for assay, each cubic centimeter of this solution is equivalent to about 1 per cent of manganese. Now add about 50 cc. of dilute 1 : 10 sulphuric acid and heat the mixture nearly to boiling with gentle agitation. Avoid shredding the filter. If the precipitate fails to dissolve completely, after boiling gently for some time, add more of the oxalic acid solution, but avoid a large and unnecessary excess. When the precipitate has entirely dissolved, dilute the solution to 150–200 cc. with hot water and titrate to a faint permanent pink tinge with a standard solution of potassium permanganate (8). The excess of oxalic acid not consumed by the MnO_2 is thus found. Subtracting this from the total amount of oxalic acid used, the remainder is the amount used in reducing the MnO_2 to MnO. Multiply this figure by the value of 1 cc. in manganese to obtain the amount of manganese in the ore.

Example.—Took 0.5 gram of ore.

1 cc. of the permanganate solution = 0.5611 cc. of the oxalic acid sol.

1 cc. of the oxalic acid solution = 0.00502 gram of manganese, or, 1.04 per cent when 0.5 gram of ore is taken.

Permanganate used in titrating excess of oxalic acid, 5.65 cc., equivalent to 3.17 cc. of oxalic acid solution.

Total number of cc. of oxalic acid solution used . .	25.40
Less excess	3.17
Consumed by the MnO_2	22.23

22.23 multiplied by 1.04 gives 23.12, the percentage of manganese in the ore.

* Fifty cc. are sufficient in any case.

7. The reactions that take place may be expressed as follows: Between the MnO_2 and the oxalic acid:

$$MnO_2 + C_2O_4H_2.2H_2O + H_2SO_4 \rightarrow MnSO_4 + 2CO_2 + 4H_2O.$$

Thus 126.058 parts, by weight, of oxalic acid in the standard solution correspond to 54.93 parts of manganese. One per cent of manganese, on the basis of 0.5 gram of ore taken for assay, is 0.005 gram, and the amount of oxalic acid corresponding to this is 0.01148 gram. This, then, is the amount to be contained in 1 cc., or, 11.48 grams per liter, in order that 1 cc. = 1 per cent Mn.

Between the oxalic acid and permanganate:

$$2KMnO_4 + 5C_2O_4H_2 . 2H_2O + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 10H_2O.$$

The standard solutions required are prepared as follows:

8. **Standard Potassium Permanganate.**—This may be approximately one-tenth normal, or about 3.16 grams per liter. The solution used for iron is ordinarily employed. The iron value multiplied by 1.129 will give the oxalic acid value.[4] This value may also be determined by standardizing against oxalic acid or an oxalate directly. While the usual C. P. oxalic acid is not absolutely pure, it will generally suffice for technical work. Weigh carefully about 0.2 gram of the clean crystals and dissolve in a 6-oz. flask in a mixture of about 5 cc. of strong sulphuric acid and 100 cc. of water. Heat to 60°–70° C. and titrate with the permanganate solution to a permanent faint pink tinge. From the number of cubic centimeters used, calculate the value of 1 cc. in oxalic acid.

Example.—Took 0.2195 gram of oxalic acid. Used 34.0 cc. of permanganate. Then $0.2195 \div 34.0 = 0.006455$, the value in grams of oxalic acid of 1 cc. of the permanganate solution. One cc. of an exactly decinormal permanganate solution would equal 0.0063029 gram of oxalic acid.

9. **Standard Oxalic Acid Solution.**—This, as explained above (7), should contain about 11.48 grams of $C_2O_4H_2 . 2H_2O$ per liter, in order that 1 cc. may equal about 1 per cent of manganese when 0.5 gram of ore is taken for assay. Standardize as follows: Place in an 8-oz. flask about 5 cc. of strong sulphuric acid and dilute with 100 cc. of water. From a burette run in about 25 cc. of the oxalic acid solution. Heat

the mixture to about 70° C. and titrate with the standard permanganate to a permanent faint pink tinge. From the number of cubic centimeters of permanganate used, and the known value of each cubic centimeter in oxalic acid, calculate the true strength of the oxalic acid solution and the consequent value of 1 cc. in manganese.

Example.—Ran in 21.70 cc. of oxalic acid solution. Used 40 cc. of permanganate. If the value of 1 cc. of permanganate is 0.006455 gram of $C_2O_4H_2 . 2H_2O$, then the 40 cc. used are equal to 0.2582 gram. As this is the amount of oxalic acid contained in 21.70 cc., each cubic centimeter contains 0.0119 gram. In the reaction between manganese dioxide and oxalic acid previously given (7), it is shown that 126.058 parts by weight of oxalic acid are equal to 54.93 parts of manganese. Consequently, to find the manganese value of the present oxalic acid, we have the proportion.

$$126.058 : 54.93 = 0.0119 : x$$
$$x = 0.005184$$
$$(\text{Oxalic acid} \times 0.4357 = \text{Mn}).$$

1 cc. of the oxalic acid solution therefore equals 0.005184 gram of Mn, or, 1.037 per cent on the basis of 0.5 gram of ore.

10. In determining the manganese value of the oxalic acid solution, the value of 1 cc. of the permanganate solution in cubic centimeters of standard oxalic acid solution should also be noted. Thus, in the last example, 40 cc. of permanganate solution were equal to 21.70 cc. of oxalic acid solution, therefore, 1 cc. of permanganate solution is equal to 0.5425 cc. of oxalic acid solution. This value should be marked on the permanganate bottle. The oxalic acid solution very slowly decomposes on keeping and requires to be restandardized occasionally. The addition of 50 cc. of sulphuric acid per liter greatly improves its keeping qualities.

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[1] In this method the manganese is precipitated in the form of MnO_2. This is filtered off and subsequently reduced to MnO by oxalic acid in the presence of dilute sulphuric acid. The MnO dissolves in the sulphuric acid to form $MnSO_4$. The oxalic acid is added in the shape of a known volume of a standard solution, and the amount consumed in the reduction is determined by titrating the remainder with permanganate and deducting the amount found from the total added. From the amount of oxalic acid required for the reduction the manganese is calculated in accordance with the following reaction:

$$MnO_2 + C_2O_4H_2 \rightarrow MnO + H_2O + 2CO_2.$$

Every molecule of $C_2O_4H_2$ is thus equivalent to 1 atom of Mn. The crystallized acid used in making the standard solution holds, of course, the same relation. Its formula is $C_2O_4H_2.2H_2O$, and its molecular weight is 126.058. Mn = 54.93. 126.058 parts by weight of oxalic acid crystals therefore = 54.93 parts by weight of Mn. The Mn value of 1 cc. of the standard oxalic acid solution is thus easily calculated.

[2] Any lead not removed would be precipitated by the bromine as PbO_2 and eventually count as manganese.

[3] The following reaction gives the outline of how the bromine oxidizes and precipitates the manganese:

$$MnO + 2Br + H_2O \rightleftharpoons MnO_2 + 2HBr.$$

If the HBr were allowed to accumulate, the reaction might reverse as follows:

$$2HBr + MnO_2 \rightarrow MnBr_2 + 2H_2O + 2Br.$$

This is prevented by the sodium acetate added. It neutralizes the hydrobromic acid and sets free acetic acid in its place. The acetic acid is without action on the precipitated MnO_2.

[4] Oxalic acid is oxidized to carbon dioxide and water as follows: $C_2O_4H_2 + O \rightarrow 2CO_2 + H_2O$. This shows that 1 oxygen is sufficient for 1 molecule of $C_2O_4H_2$, or of the crystallized acid, $C_2O_4H_2.2H_2O$, the molecular weight of which is 126,058.

When ferrous iron is oxidized, it is changed from FeO to Fe_2O_3, as follows: $2FeO$, or, $Fe_2O_2 + O = Fe_2O_3$. Thus $Fe_2 = O$. Accordingly, $C_2O_4H_2.2H_2O = O = Fe_2$, that is, by weight, 126.058 parts of crystallized oxalic acid = 111.68 parts of Fe. This gives 1 Fe = 1.129 oxalic acid, or, the Fe value of the permanganate multiplied by 1.129 will give the oxalic value.

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11. Determination of MnO_2 Only.—Place 0.5 gram of the finely ground ore in an 8-oz. flask. Add 25 cc. of water, 5 cc. of strong sulphuric acid and as much of the usual standard oxalic acid solution delivered from a burette, as may be judged necessary to decompose the MnO_2 present and leave a moderate excess of oxalic acid. More may be added later if found necessary. Boil gently until the decomposition of all MnO_2 is effected, adding more water or more oxalic acid solution as required. Finally, dilute, if necessary, with hot water, until the flask is about half full, and titrate with permanganate as usual. Make the same calculation as in **6**. Multiply the per cent of manganese shown by 1.582 to obtain the per cent of MnO_2.

12. Volhard's Method.—This is the method most generally used in western laboratories, but not my personal preference. Treat 1 gram of the ore in an 8-oz. flask with whatever acids are necessary to decompose it, beginning with 10 cc. of strong hydrochloric acid, and heating

very gently, if oxides are present, and afterwards adding nitric acid, if necessary, to decompose sulphides and peroxidize iron. When the decomposition is complete add about 7 cc. of strong sulphuric acid and heat over a free flame until fumes of sulphuric acid are evolved copiously. Cool, add 25 cc. of water, boil a short time, and allow to stand, hot, with frequent shaking, until all anhydrous ferric sulphate has dissolved. Transfer the mixture * to a 500-cc. graduated flask and add an emulsion of zinc oxide † in slight excess, to precipitate the iron. Agitate the flask to facilitate the precipitation and see that a slight excess of zinc oxide remains when the reaction is complete. Now dilute the contents of the flask up to the mark with cold water, mix thoroughly and allow to stand a short time and partially settle. By means of a graduated pipette draw off 100 cc. of the clear supernatant liquid and transfer it to an 8-oz. flask. While the precipitate in the 500-cc. flask may appear large, it actually occupies but a very small space, and any error caused by it may consequently be neglected. Likewise the error in measurement due to change of temperature during the manipulation is insignificant. Heat the solution in the small flask to boiling, add two or three drops of nitric acid (which causes the subsequent precipitate to settle more quickly) and titrate with a standard solution of potassium permanganate. The permanganate causes a precipitate which obscures the liquid, and it is therefore necessary to titrate cautiously and agitate the flask after each addition, and then allow the precipitate to settle sufficiently to observe whether or not the solution is colored pink. A little experience will enable one to judge, by the volume of the precipitate formed, about how rapidly to run in the permanganate. The final pink tinge, indicating the end of the reaction, is best observed by holding the flask against a white background and observing the upper edges of the liquid. When this point is attained, bring the contents of the flask nearly to a boil once more and again observe if the pink tint still persists, adding more permanganate if necessary. In making this end-test avoid actually boiling the liquid, as a continual destruction of the color may sometimes thus be effected and the true end-point considerably passed. When the color thus remains permanent the operation is ended. Observe the

* Using hot water.

† For ordinary use I simply mix the usual C. P. zinc oxide with water. A better and purer mixture is made as follows: Precipitate a solution of pure zinc sulphate with a solution of potassium hydroxide in insufficient amount to cause the solution to become alkaline. Wash the residue several times with hot water and then transfer it to a tightly stoppered bottle with enough water to hold it in suspension.

number of cubic centimeters of permanganate solution used and calculate the result.

13. The precipitate formed is not necessarily manganese dioxide, although the calculation can be correctly made as though the following reaction took place:

$$3MnSO_4 + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO + 2H_2SO_4.$$

In the presence of metallic salts, such as those of calcium or zinc, manganites of varying composition are formed, e.g.,

$$4KMnO_4 + 5ZnSO_4 + 6MnSO_4 + 14H_2O \rightarrow 4KHSO_4 + 7H_2SO_4 + 5(ZnH_2O_2 \cdot 2MnO_2).$$

The precipitated manganese is, however, always in the tetravalent form, and, therefore, the ratio of the first reaction between the manganese and the permanganate is not changed.

14. It is customary to use the same permanganate solution for both iron and manganese. After the factor for iron has been determined (IRON, 12) it may be multiplied by 0.2952 to obtain the factor for manganese. It will be observed in the first equation above that $2KMnO_4$ are required for 3Mn, and in the reaction for iron in IRON, 2, that $2KMnO_4$ are required for 10Fe. Therefore 558.4 parts of iron are equivalent to 164.79 parts of manganese, or, 1 part of iron to 0.2952 part of manganese.[1]

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[1] In the iron titration in an acid solution, the Mn_2O_7 of the permanganate, $K_2O.Mn_2O_7$, is wholly reduced to Mn_2O_2, or 2MnO, by giving up O_5. In the present manganese titration the solution is neutral and the Mn_2O_7 of the permanganate is reduced only to Mn_2O_4, or, $2MnO_2$ and gives up only O_3.

In the manganese titration, then, the permanganate has only three-fifths of the oxidizing power it has in the iron titration.

When ferrous iron is oxidized, $Fe_2O_2 + O = Fe_2O_3$, making $Fe_2 = O$. In the case of manganese, $MnO + O = MnO_2$, making $Mn = O$. This gives $Fe_2 = Mn$, or, 111.68 Fe = 54.93 Mn, making 1 Fe = 0.4920 Mn. But as permanganate has, in the present case, only three-fifths of the oxidizing power it has in the case of iron, then the Mn ratio is $\frac{3}{5}(0.4920)$, or 0.2952.

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15. The Bismuthate Method for the Determination of Manganese.*—This method is based on the fact that a manganous salt

* Andrew A. Blair, Jour. Am. Chem. Soc., XXVI, 793. Method originally proposed by Schneider and modified first by Reddrop and Ramage and then by Brearley and Ibbotson.

in the presence of an excess of nitric acid is oxidized to permanganic acid by bismuth tetroxide. The permanganic acid formed is very stable in nitric acid of 1.135 sp. gr. when the solution is cold, but in hot solutions the excess of the bismuth tetroxide is rapidly decomposed and then the nitric acid reacts with the permanganic acid, and as soon as a small amount of manganous salt is formed the remainder of the permanganic acid is decomposed, manganous nitrate dissolves and manganese dioxide precipitates.

In the cold, however, the excess of the bismuth salt may be filtered off, and to the clear filtrate an excess of ferrous sulphate may be added and the amount necessary to deoxidize the permanganic acid determined by titrating with permanganate. The end reactions are very sharp and the method is extremely accurate, but the presence of even a trace of hydrochloric acid utterly vitiates the results. Reddrop and Ramage pointed out that bismuth tetroxide, which was used by Schneider, is difficult to obtain free from chlorides, and they recommended sodium bismuthate, which they prepare as follows: Heat 20 parts of caustic soda nearly to redness in an iron or nickel crucible and add, in small quantities at a time, 10 parts of basic bismuth nitrate, previously dried in a water-oven. Then add 2 parts of sodium peroxide and pour the brownish-yellow fused mass on an iron plate to cool; when cold, break it up in a mortar, extract with water and collect on an asbestos filter. The residue, after being washed four or five times by decantation, is dried in the water-oven, then broken up and passed through a fine sieve. (The Baker & Adamson Chemical Co. have prepared sodium bismuthate in this manner which is perfectly free from manganese chlorides and has proved entirely satisfactory.)

THE METHOD

Steels.—Dissolve 1 gram of drillings in 50 cc. of nitric acid (sp. gr. 1.135) in an Erlenmeyer flask of 200 cc. capacity. Cool and add about 0.5 gram of bismuthate. The bismuthate may be measured in a small spoon, and experience will soon enable the operator to judge of the amount with sufficient accuracy. Heat for a few minutes, or until the pink color has disappeared, with or without the precipitation of manganese dioxide. Add sulphurous acid, solution of ferrous sulphate or sodium thiosulphate in sufficient amount to clear the solution and heat until all nitrous oxide has been driven off. Cool to about 15° C., add

an excess of bismuthate and agitate for a few minutes. Add 50 cc. of water containing 30 cc. of nitric acid to the liter and filter through an asbestos felt on a platinum cone into a 300-cc. Erlenmeyer flask, and wash with 50 to 100 cc. of the same acid. The arrangement shown in Fig. 16 has proved very satisfactory. Run into the flask from the pipette, shown in Fig. 17, a measured volume of ferrous sulphate solution and titrate to a faint pink color with permanganate. The number of cubic centimeters of the permanganate solution obtained, subtracted from the number corresponding to the volume of ferrous sulphate solution used, will give the volume of permanganate equivalent to the manganese in the sample, which, multiplied by the value of the permanganate in manganese, gives the amount of manganese in the steel.

FIG. 16.

Pig Iron.—Dissolve 1 gram in 25 cc. of nitric acid (sp. gr. 1.135) in a small beaker, and as soon as the action has ceased, filter on a 7-cm. filter into a 200-cc. Erlenmeyer flask, wash with 30 cc. of the same acid and proceed as in the case of steels.

In the analysis of white irons it may be necessary to treat the solution several times with bismuthate to destroy the combined carbon. The solution, when cold, should be nearly colorless; if it is not, another treatment with bismuthate is necessary.

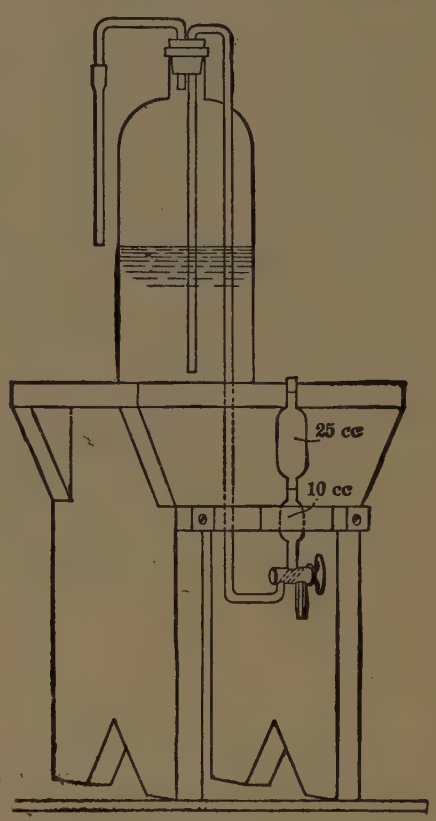

FIG. 17.

Iron Ores Containing Less than 2 Per Cent of Manganese.—Treat 1 gram in a platinum dish or crucible with 4 cc. of strong sulphuric acid, 10 cc. of water and 10 to 20 cc. of hydrofluoric acid. Evaporate until the sulphuric acid fumes freely. Cool and dissolve in 25 cc. of 1.35 nitric acid. If no appreciable residue remains, transfer to a 200-cc. Erlenmeyer flask, using 25 cc. of 1.135 nitric acid to rinse the dish or crucible, and proceed as usual. If there is an appreciable residue, filter on a small filter into a beaker, wash with water, burn the

filter and residue in a crucible, and fuse with a small amount of potassium acid sulphate. Dissolve in water with the addition of a little nitric acid, add to the main filtrate, evaporate nearly to dryness, take up in 1.135 nitric acid and transfer to the flask as before.

Manganese Ores and Iron Ores High in Manganese.—Treat 1 gram as in the case of iron ores, using a little sulphurous acid if necessary. Transfer the solution to a 500-cc. flask, dilute to the mark, mix thoroughly and measure into a flask, from a carefully calibrated pipette such a volume of the solution as will give from 1 to 2 per cent of manganese and enough strong nitric acid (sp. gr. 1.4) to yield a mixture of 1.135 acid in a volume of 50 to 60 cc. For example, in a 50 per cent ore use 10 cc. of the solution and add 30 cc. of water and 10 cc. nitric acid (sp. gr. 1.4). In this case the manganese must be calculated on $\frac{1}{50}$ of a gram or 20 mg. of ore. When working on such amounts it is always desirable to make duplicate analyses and take the mean, as a difference of 0.1 cc. makes a large error in the result. When the ore contains a much smaller amount of manganese, say 5 to 10 per cent, it is better to make up the solution to 100 cc. instead of 500.

Ferro-manganese.—Treat 1 gram exactly like steel. Dilute to 500 or 1000 cc. and proceed as in manganese ores.

Ferro-silicon.—Treat 1 gram with sulphuric and hydrofluoric acids and proceed as with iron ores.

Special Steels.—Steels containing chromium offer no special difficulties except that it must be noted that while in hot solutions the chromium is oxidized to chromic acid, which is reduced by the addition of sulphurous acid, the oxidation proceeds so slowly in cold solutions that if there is no delay in the filtration and titration the results are not affected. Steels containing tungsten are sometimes troublesome on account of the necessity for getting rid of the tungstic acid. Those that decompose readily in nitric acid may be filtered and the filtrate treated like pig iron, but when it is necessary to use hydrochloric acid it is best to treat with *aqua regia*, evaporate to dryness, redissolve in hydrochloric acid, add a few drops of nitric acid, dilute, boil, and filter. Get rid of every trace of hydrochloric acid by repeated evaporations with nitric acid, and proceed as with an ordinary steel.

REAGENTS

Nitric Acid (*sp. gr.* 1.135).—A mixture of 3 parts of water and 1 part strong nitric acid answers perfectly for this purpose.

Nitric Acid (*3 per cent*).—Thirty cc. of strong nitric acid to the liter.

Permanganate Solution and Ferrous Sulphate Solution.—One gram of potassium permanganate to the liter gives a solution of convenient strength, and 12.4 grams of ferrous ammonium sulphate and 50 cc. of strong sulphuric acid,* made up to 1 liter, gives a solution which is almost exactly equal to the permanganate solution. As the strength of the ferrous sulphate solution changes quite rapidly, while the permanganate remains unaltered for months, it is unnecessary and troublesome to attempt to keep them of the same strength. If a constant volume of the ferrous sulphate solution is used and tested against the permanganate solution every day, the calculation of the results is very simple. It is necessary that the conditions should be the same in getting the strength of the ferrous sulphate solution as in titrating a solution for manganese, and after many experiments the following method of procedure was adopted: Measure into a 200-cc. flask 50 cc. of nitric acid (sp. gr. 1.135), cool and add a very small amount of bismuthate, dilute with 50 cc. of 3 per cent nitric acid, filter into a 300-cc. flask and wash with 50 cc. of 3 per cent nitric acid. If the felt is well coated with bismuthate it is unnecessary to add any to the nitric acid in the flask, as filtration through the mass of bismuthate on the felt will answer the purpose. Run in from the pipette (Fig. 17) 25 cc. of ferrous sulphate solution and titrate with the permanganate to a faint pink. This gives the value in permanganate of the ferrous sulphate solution. With this method of procedure the discrepancies that had occurred entirely disappeared, and it is possible to make any number of determinations with a variation of less than 0.1 cc.

The permanganate solution may be standardized in three ways:

First, by getting its value in iron in the usual way and calculating its value in manganese. The proportion is 279.2 : 54.93, or as 1 : 0.1967.

Second, by titrating a steel with a known amount of manganese and getting the value of the solution by dividing the percentage

* Dr. C. B. Dudley proposes to use 25 cc. of sulphuric and 25 cc. of strong phosphoric acid as tending to give a more nearly colorless solution.

of manganese by the number of cubic centimeters of the permanganate used.

Third, by making a solution of pure manganese sulphate and determining the manganese in it by evaporating a weighed amount of the solution to dryness, heating to dull redness and weighing as manganese sulphate, which, multiplied by 0.3639 gives the amount of manganese. Five grams of " C. P." manganese sulphate dissolved in 500 cc. of water and filtered will give a solution containing about 0.0035 gram of manganese to the gram of solution. Weigh 1 to 3 grams of the solution in a crucible, transfer to a 200-cc. flask, using 50 cc. of nitric acid (sp. gr. 1.135), cool, add 0.5 to 1 gram bismuthate and allow it to stand for three or four minutes, shaking at intervals. Add 50 cc. of 3 per cent nitric acid and filter through the asbestos filter and wash with 50 or 60 cc. of the same acid. Run 25 cc. of the ferrous sulphate solution into the flask from the pipette and titrate with the permanganate solution to a faint pink. Subtract the number of cubic centimeters of the permanganate solution obtained from the value of the 25 cc. of ferrous sulphate solution in permanganate and the result is the number of cubic centimeters of the permanganate corresponding to the manganese in the manganese sulphate solution used. Divide the weight of the manganese in the manganese sulphate used, by the number of cubic centimeters of permanganate, and the result is the value of 1 cc. of permanganate in manganese.

Example.—One gram manganese sulphate solution contains 0.003562 gram manganese; 2.0372 grams manganese sulphate solution equals 0.0072565 gram manganese; 25 cc. ferrous sulphate solution equals 24.5 cc. permanganate solution; 2.0372 grams manganese sulphate, after oxidation and addition of 25 cc. ferrous sulphate solution, require 3.6 cc. permanganate solution; 24.5 cc. -3.6 cc. $=20.9$ cc.; 0.0072565 divided by $20.9 = 0.0003472$, or 1 cc. of permanganate equals 0.0203472 gram of manganese. If, then, 1 gram of steel, after oxidation and addition of 25 cc. ferrous sulphate solution, requires 6.2 cc. permanganate solution to give the pink color, $24.5 - 6.2 = 18.3 \times 0.0003472 = 0.006354$ gram, or the sample contains 0.635 per cent manganese.

NOTES AND PRECAUTIONS

The delicacy of the reaction of manganese in nitric acid solution with sodium bismuthate is extraordinary; 0.000005 gram of manganese gave an appreciable color in 50 cc. of solution.

When the proper precautions are observed, this method for materials containing small amounts of manganese, say up to 2 per cent, is more accurate than any other method, volumetric or gravimetric, that I have ever used.

As will be seen in the description of the various methods of solution, the use of hydrochloric acid has been avoided because the presence of even traces of this reagent is fatal to the accuracy of the method. Where it is impossible to avoid its use and its presence is suspected in the final nitric acid solution, the addition of a drop or two of silver nitrate will overcome the difficulty, but the filter must be rejected after using it for filtering a solution so treated.

Any form of asbestos filtering tube may be used for filtering off the bismuthate, but the perforated cone with bell jar, shown in Fig. 16, is the most satisfactory, because it has the largest area of filtering surface. One filter may be used for fifty or more determinations and the time occupied in filtering and washing one determination is only from one minute and a half to three minutes. The filtrate must be perfectly clear, for the least particle of bismuthate carried through will vitiate the result by reacting with the excess of ferrous sulphate. As soon as the filtration and washing are completed, the ferrous sulphate should be added and the excess titrated with the permanganate solution, as the permanganic acid gradually decomposes on standing and the warmer the solution the more rapid is the decomposition. At a temperature of 5° C. the solution will remain unaltered for several hours, but at 40° C. fifteen minutes will show an appreciable change. The larger the amount of manganese the more rapid the change. It is especially important not to allow the solution to stand after adding the ferrous sulphate, as the excess of this reagent reacts with the nitric acid in a few minutes and the formation of the smallest amount of nitrous oxide is fatal to the accuracy of the determination. For this reason it is important to boil off every trace of nitrous oxide when in the earlier part of the operation sulphurous acid or other deoxidizing agent is added.

When working with steels of unknown manganese content, it may

often happen that 25 cc. of ferrous sulphate solution are insufficient to entirely reduce the permanganic acid, in which case an additional amount of ferrous sulphate must be added. The pipette shown in Fig. 17 has been arranged to meet this contingency. It will be noticed that the solution of permanganic acid upon the addition of an insufficient amount of ferrous sulphate does not necessarily retain its pink or purple color, but usually changes to a dirty brown. When this occurs, the lower part of the pipette may be emptied directly into the flask and the value of the two parts taken as the amount from which the number of cubic centimeters of permanganate corresponding to the excess of ferrous sulphate must be subtracted. When the sample is low in manganese, the 10-cc. portion of the pipette alone may be used, so that the arrangement allows a great deal of variation in the manganese content of the samples worked on.

There is no advantage in using permanganate solutions differing in strength from the one given above, but the strength of the ferrous sulphate solution may be changed to meet special cases.

CHAPTER XIX

MERCURY

1. Volumetric Method.*—Weigh 1 gram, more or less, of the ore according to richness, into an 8-oz. flask. Add 10 cc. of 1 : 1 sulphuric acid and about 0.5 gram of potassium permanganate crystals. Agitate the flask and heat to boiling, finally boiling to fumes. Allow to cool, then dilute with about 50 cc. of cold water, heat to boiling, and, while boiling, add oxalic crystals, a little at a time, until the separated MnO_2 is all reduced and dissolved. Cool under the tap and filter, washing with dilute (1 : 10) sulphuric acid.

Pass hydrogen sulphide into the cold filtrate to saturation. Filter, washing with cold water. Rinse the precipitate from the filter, while still in the funnel, as completely as possible, into a porcelain dish or casserole and boil it for some time with dilute nitric acid (sp. gr. 1.2–1.3.)† Finally, dilute the mixture with a little hot water and filter through the same filter as before, washing with hot dilute nitric acid (1 : 3). The filter will probably be more or less stained with sulphides that could not be rinsed off. The hot filtration and washing will tend to cleanse these traces of sulphides, so that any impurities finally left with the HgS will be negligible.

2. Wash the well-washed sulphide from the filter into an 8-oz. flask, with hot water, using as little as possible. The stain remaining on the filter may usually be neglected. Save the filter, however. To the mixture in the flask add 5–6 cc. of strong sulphuric acid and 0.5 gram, or usually less, of potassium permanganate crystals. Boil with frequent agitation over a free flame, to fumes. Now remove from the heat, and, without cooling, add oxalic crystals, in very small portions so as to avoid much excess, until all the separated MnO_2 is reduced and dissolved. Again heat to fumes to destroy the excess of oxalic acid.

* A. H. Low, Chemist–Analyst, 1919, 29, 13.

† A mixture of 2 parts of strong acid to 1 part of water will serve.

Cool and then dilute with about 100 cc. of cold water. The solution should be perfectly clear.

3. Cool to room temperature, add the usual ferric indicator (about 5 cc. of a strong solution of ferric ammonium sulphate, acidified with nitric acid to decolorize) and titrate with standardized, approximately 1/10 normal, thiocyanate solution to the usual faint brownish tint. One cc. 1/10 normal thiocyanate = 0.01003 gram Hg.

Standardize the thiocyanate as described in CHLORINE, 3, or ARSENIC, 7.

If the stain on the filter paper is worth recovering, spread the wet paper on a watch-glass, sprinkle on a little powdered permanganate, add a little 1 : 1 sulphuric acid and warm a moment. Now add a very little dry oxalic acid, warm again to dissolve any MnO_2 and then rinse the solution into the flask containing the balance of the sulphide, continuing as above in **2**.

4. **Eschka's Method.***—*Particularly applicable to low-grade ores.*—Mix 0.2 to 2 grams of the ore with 1–4 grams of iron filings in a porcelain crucible of suitable size. Prepare a dish-shaped cover of thin sheet gold for the crucible. This cover should be of such a form that it can be kept cool by being filled with water; it should be large enough to project somewhat over the edge of the crucible, to prevent any mercury from escaping. Place the crucible in a ringstand, put on the weighed cover and nearly fill it with water. Carefully heat the lower part of the crucible with a Bunsen burner, but keep the upper part cool. A ring of thin asbestos board fitted around the crucible at the proper height will assist materially in preventing the top from getting overheated. Add cold water to the cover from time to time. It will require from ten to thirty minutes to distill off the mercury. When the operation is considered ended, remove the gold cover, dip in alcohol, dry carefully without heating and weigh. The increase over the original weight represents the mercury. A silver cover appears to answer practically as well as one of gold.

Notes.—Instead of filling the cover with water, a small metal dish containing water may be placed upon it. The dish should have a curved bottom, over which the silver or gold cover has been shaped. It is a good plan also to give the edge of the cover a reverse curve, to make it fit snugly over the top edge of the crucible.

It is best to have a thin layer of iron filings over the charge.

* Zeit. f. Anal. Chem., Vol. 11, p. 344.

Sulphide ores containing arsenic are best mixed with double their weight of a mixture of 4 parts zinc oxide and 1 part sodium carbonate, together with iron filings 5 times the weight of the ore.

5. Wet Method.—*Applicable to cinnabar ores not containing appreciable amounts of other reducible metallic compounds.*

Treat 1–5 grams of the ore, according to its supposed richness, in a covered porcelain dish with sufficient *aqua regia* to decompose it. Heat gently until decomposition is complete, and then remove and wash the cover and evaporate the solution to dryness on a water-bath. Take up the residue in strong hydrochloric acid and again evaporate to dryness to expel all of the nitric acid. Again dissolve in hydrochloric acid, dilute sufficiently and filter. To the filtrate add an excess of a clear stannous chloride solution containing an excess of acid (which may be made by dissolving tin in an excess of hydrochloric acid), and boil the mixture for a short time. The mercuric chloride is reduced to finely divided metallic mercury. Allow the precipitate to settle completely and then decant the clear liquid carefully. Unite the precipitate into one globule by heating it with a little moderately dilute hydrochloric acid mixed with a few drops of stannous chloride. Wash the mercury by decantation, first with water slightly acidified with hydrochloric acid, and then with pure water and then transfer it to a weighed porcelain crucible. Absorb as much of the adhering water as possible with the filter-paper and then place the crucible in a desiccator over sulphuric acid. When perfectly dry, weigh as metallic mercury.

The results obtained by this method are certain to be somewhat low, owing to the impossibility of evaporating the hydrochloric acid solutions to dryness, in driving off the nitric acid, without volatilization of some mercuric chloride with the escaping steam. As a technical method, however, for low-grade cinnabar ores it answers very well.

6. Dry Method.—*Applicable to all ores.*—Prepare a combustion-tube about 18 or 20 in. long and sealed at one end. Place in the closed end a column of crushed magnesite about 4 in. long, then add a section of about 2 in. of freshly ignited caustic lime, then about 4 in. of an intimate mixture of a weighed portion of the ore with an excess of caustic lime, rinsing out the mortar with a little lime and adding this also, and then about 2 in. of caustic lime. Finally, insert against the whole a loose plug of asbestos about 2 in. long. Now draw out the end of the tube to a narrow opening and bend it at right angles. Tap

the tube horizontally on the table, gently, so as to leave a free passage for gases throughout its length. Place the tube in a combustion furnace and arrange a small flask partly filled with water so that the point of the tube just touches the water, which thus closes it. Now proceed to heat the tube, beginning at the end containing the asbestos and gradually approaching the other end, until the tube is red-hot throughout the entire portion in the furnace. The carbon dioxide evolved from the magnesite serves to sweep out the last traces of mercury vapor into the water. While the tube is still hot, cut off the point above the flask and rinse any condensed mercury into the water. Agitate the flask so as to collect the mercury into one globule, and, after allowing to stand and settle some time, decant off the perfectly clear water and transfer the mercury to a weighed porcelain crucible. Remove as much of the adhering water as possible with filter-paper and then dry the mercury to constant weight over sulphuric acid in a desiccator. It must not be heated.

7. Krieckhaus' Volumetric Method.*—Weigh 2 grams of the ore into a 150-cc. beaker. Add 2 cc. of strong nitric acid and 10 cc. of strong hydrochloric acid. Measure the nitric acid first and then measure the hydrochloric without washing the glass. This ensures getting all of the nitric acid, which is essential, although an excess must be avoided.

Allow to stand cold for an hour or more, when all the mercury will be in solution; or, to save time, heat slightly but not to boiling. Now dilute with 10–15 cc. of water, heat nearly to boiling and filter into a 300-cc. Erlenmeyer flask, washing with hot water. To the filtrate, which contains the mercury (and need not be much over 100 cc. in volume), add 60 cc. of stannous chloride solution (prepared as described below), cork the flask and allow to stand, tilted at an angle of about 45°, until all the mercury has settled and the liquid is clear. The settling takes about two hours.

Decant the liquid and then fill the flask about two-thirds full with cold water, slightly acidulated with sulphuric acid to prevent the separation of basic tin salts. Again allow to settle with the flask tilted as before. If any mercury floats, a jet of water will cause it to settle. In about ten minutes, decant the clear liquid as completely as possible. Dissolve the precipitated mercury in 2 or 3 cc. of strong nitric acid,

* Kindly furnished by Mr. Leon L. Krieckhaus. The results sent by Mr. Krieckhaus agree closely with those he obtained by Eschka's method.

warming gently to ensure complete solution and oxidation to mercuric nitrate.

Add about 75 cc. of cold water and a few cubic centimeters of a solution of ferric nitrate, as indicator (or ferric ammonium alum slightly acidulated with nitric acid), and titrate cold with standard potassium thiocyanate solution to the usual red tinge.

8. If the potassium thiocyanate solution contains 9.69 grams of the salt per liter, 1 cc. will equal 0.01 gram of mercury, or 0.5 per cent on the basis of 2 grams of ore taken for assay. It is best to standardize it with pure silver or silver nitrate, as described in ARSENIC, **7.** The silver value of 1 cc. multiplied by 0.9298 will give the mercury value.

Prepare the stannous chloride solution by mixing 50 grams of the salt, 50 cc. of strong hydrochloric acid and 150 cc. of water, and boiling with a stick of metallic tin until clear. Keep a stick of tin in the bottle.

9. Notes by Mr. Krieckhaus.—If lead is present in an ore, it can probably be largely removed by adding a little sulphuric acid before filtering off the gangue. If any remains in solution and comes down as chloride with the mercury, the chlorine it carries will interfere, but the lead chloride could probably be washed out of the mercury with hot water. Stannous chloride precipitates copper as cuprous chloride, but this may be easily removed with dilute ammonia.

In order that the mercury shall settle well, it is best to have the solution cold and the tin solution quite strongly acid, but not saturated with stannous chloride. Add only 1 or 2 cc. of the tin solution at first and agitate the flask. This will cause a precipitation of mercurous chloride. Then add the remainder of the tin solution and allow to stand as above described. Under these conditions the mercury will settle clear in an hour or two. If the liquid is hot or the tin solution too strong, the mercury is so finely divided that it is slow to settle and difficult to wash without loss.

10. Seamon's Volumetric Method.*—Weigh 0.5 gram of the finely ground ore into an Erlenmeyer flask of 125 cc. capacity. Add 5 cc. of strong hydrochloric acid and allow it to act for about ten minutes at a temperature of about 40° C., then add 3 cc. of strong nitric acid and allow the action to continue for about ten minutes longer. All the mercury should now be in solution. Now if lead be present, add 5 cc. of strong sulphuric acid; it may be omitted otherwise. Dilute with 15 cc. of water and then add ammonia cautiously until the liquid is

* Manual for Assayers and Chemists, p. 112.

slightly alkaline. Bismuth, if present, will precipitate. Acidify faintly with nitric acid, filter, receiving the filtrate in a beaker, and wash thoroughly.

Add to the filtrate 1 cc. of strong nitric acid that has been made brownish in color by exposure to the light, and titrate with a standard solution of potassium iodide until a drop of the liquid brought into contact with a drop of starch liquor, on a spot-plate, shows a faint bluish tinge. It is a good plan to set aside about one-third of the mercury solution and add it in portions as the end-point is successively passed, finally rinsing in the last portion and titrating to the end-point very carefully.

Deduct 0.5 cc. from the burette reading and multiply the remaining cubic centimeters used by the percentage value of 1 cc. in mercury to obtain the percentage in the ore.

The standard potassium iodide solution should contain 8.3 grams of the salt per liter. Standardize against pure mercuric chloride. Dissolve a weighed amount of the salt in water, add 2 cc. of the discolored nitric acid and titrate as above. One cc. of the standard solution will be found equivalent to about 0.005 gram of mercury, or about 1 per cent on the basis of 0.5 gram of ore taken for assay.

The precipitate of red mercuric iodide which forms during the titration may not appear if the amount of mercury present is very small, but this failure to precipitate does not appear to affect the result.

Iron, copper, bismuth, antimony and arsenic, when added separately to the ore, did not influence the results in Seamon's tests. Silver interferes. Duplicate results should check within 0.1–0.2 of 1 per cent.

CHAPTER XX

MOLYBDENUM

1. High-grade Ores and Concentrates.—Weigh 0.5 gram of the finely ground material. Place in a thin spun-iron crucible of about 25–30 cc. capacity and mix with 1 gram of sodium carbonate. Add about 6 grams of sodium peroxide and again mix well.

Holding the crucible with tongs, fuse over a Bunsen burner, heating slowly at first and gradually bringing to dull redness. Rotate the crucible as the mixture melts, so as to obtain a perfect fusion without overheating and destroying the crucible. A low red heat is all that is necessary. With a bright red the iron is liable to be strongly attacked and the crucible perforated. The initial melting of the mass is slow, but a low red heat, persisted in, will eventually bring it to perfect fluidity.

The same crucible should serve for many fusions (cf. CHROMIUM, **2**). The sodium carbonate is used solely to moderate the action of the peroxide. With oxidized material it is unnecessary, but without it sulphides may scintillate and spatter, or even deflagrate. Add more or less than 1 gram, according to judgment or trial.

2. After the fusion, allow to cool to a crust on top and then set the crucible in a 400-cc. beaker containing about $\frac{3}{4}$ in. of cold water. Cover the beaker and then upset the crucible with a glass rod. Disintegration usually occurs quickly without further heating. Remove and rinse the cover and then lift out the crucible with the glass rod and wash it.

Add 10 grams of ammonium carbonate, which should be sufficient to neutralize all the fixed alkali and leave an excess.[1] Warm until the ammonium carbonate is all dissolved and then filter (best with a Witt's plate and suction) and wash at least ten times with hot water.

Add about 2 grams of tartaric acid or a tartrate (Rochelle salts) to the filtrate, which should still remain strongly alkaline. This is to

prevent precipitation of tungsten or vanadium when the solution is subsequently acidified.

3. Saturate the alkaline liquid with hydrogen sulphide, and then make slightly acid with dilute (1 : 1) sulphuric acid. Filter off the molybdenum sulphide and wash five or six times with hot water. The filtrate may still contain a little molybdenum.* Make it strongly alkaline with ammonia and again saturate with hydrogen sulphide, then acidify and filter as before, using a second filter.

Place both filters and their contents in a large beaker and add 20 cc. of water, 10 cc. of strong nitric acid and about 2 grams of potassium chlorate. Cover the beaker and warm until solution of the molybdenum is complete. Rotate the liquid occasionally, to facilitate complete solution, but avoid vigorous stirring or such prolonged heating or concentration as would reduce the filters to a fine pulp, which might be very difficult to filter. Dilute somewhat and then filter into an 8-oz. flask, washing the residue ten times with hot water.

4. Add 5 cc. of strong sulphuric acid to the filtrate and boil down to strong fumes. This should oxidize all organic matter dissolved from the filters and expel the nitric acid.

After cooling, take up the residue in about 150 cc. of warm water, and add 3 cc. of a 4 per cent solution of copper sulphate. Now cautiously add, a little at a time at first, 5 grams of 30-mesh zinc and cover the flask with a watch-glass. If the action is too violent, cool the flask to prevent foaming over. Later, the flask may be warmed if necessary. Allow the action to proceed, warm, for about fifteen minutes. This should precipitate all the copper, and, incidentally, any arsenic present. Zinc alone, without added copper, will not remove all the arsenic. Now add a little sulphuric acid, to make certain that the liquid is still acid, and filter. Wash the residue with cold water.

5. To the filtrate add 20 cc. of 1 : 1 sulphuric acid. Pour the hot solution through the reductor in accordance with the directions given in 8, which are to be further followed to the end.

The Fe factor of the permanganate multiplied by 0.5732 gives the Mo factor.[2] Mo multiplied by 1.667 = MoS_2 (10/6, approximately).

6. In the absence of tungsten and vanadium, the process may be

* I have been informed that if the passage of the hydrogen sulphide is continued for about fifteen minutes after the acidification, all the molybdenum will come down with one precipitation.

shortened as follows: Boil the filtrate from the fusion down to about 150 cc. and filter off the (usually slight) precipitate that forms. Receive the filtrate in an 8-oz. flask, make slightly acid with sulphuric acid and then add 5 cc. of the strong acid in excess. Again boil down to about 150 cc., add 3 cc. of the copper sulphate solution and finish as above.

7. Low-grade Ores.—The fusion method of decomposition, described above, is the best for concentrates, which contain little silica. With ores, especially low grade, and tailings, where a large amount may have to be taken to insure accuracy, the dissolved silica may be very troublesome. It is best, in such cases, to decompose with acids in a flask, taking from 1 to 5 grams of substance, as may be deemed advisable, and acids in proportion. Nitric acid may be used first; then add hydrochloric acid, and perhaps more nitric, and boil until all dark particles have disappeared. Molybdenum concentrates might resist the acid treatment for a long while, but with finely ground ores it usually works well. Finally, boil to very small bulk, dilute with hot water, add an excess of ammonia, boil, filter and continue as above.

8. Reduction of the Molybdenum Solution.*—The reductor tube should have at least an 8-in. zinc column, $\frac{5}{8}$-in. in diameter, using 20–30 mesh amalgamated granulated zinc. The end of the reductor tube should be prolonged to reach nearly to the bottom of the receiving flask. The flask (32-oz.) should contain 30–35 cc. of ferric phosphate solution[3] and the end of the reductor tube should dip below this, so that the reduced molybdenum solution is not exposed to the air, but is oxidized at the expense of the ferric phosphate. The molybdenum solution should contain about 5 cc. of free sulphuric acid per 100 cc. and should be passed rather slowly (about five minutes) through the reductor, at a temperature of 50°–75° C. After passing the molybdenum solution, the reductor should be washed by passing 100 cc. of hot water containing 5 cc. of strong sulphuric acid, followed by hot water alone. The titration with the permanganate (of the strength generally used for iron) should be made in the warm solution immediately after reduction. With sufficient molybdenum present, the liquid in the receiving flask is red. As permanganate is added, the red slowly fades and the solution becomes colorless; then the final pink tint which follows is easily recognized. A blank should

* Reduction in the Permanganate Method for Molybdenum. Gooch, Methods in Chemical Analysis. Wiley & Sons, 1912. Pp. 424–429.

be made, beginning with 150 cc. of water and 5 cc. of sulphuric acid in an 8-oz. flask, adding the copper sulphate and zinc as in 1 and continuing as there described. The usual correction obtained in this way is about 0.20 cc. of permanganate solution.

Under the above conditions the reduction is from MoO_3 to Mo_2O_3, and is exact. The permanganate is standardized against sodium oxalate (Bureau of Standards), or oxalic acid (see Chapter on Iron), and is made the same strength as for iron determinations.

Ferric Phosphate Solution.—Dissolve 100 grams of Ferric Ammonium Sulphate in 500 cc. of water, adding 25 cc. of strong sulphuric acid, followed by 150 cc. of syrupy (85 per cent) phosphoric acid, and diluting to 1000 cc.

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[1] $(NH_4)_2CO_3 + 2NaHO \rightarrow 2NH_4HO + Na_2CO_3$.

[2] The change by oxidation of ferrous iron to ferric iron may be represented by $Fe_2O_2 + O = Fe_2O_3$. This makes $Fe_2 = O$.

The oxidation, in the case of molybdenum, is represented by $Mo_2O_3 + O_3 = Mo_2O_6$, or, $2MoO_3$. This makes $Mo_2 = O_3$.

If $Fe_2 = O$, then $Fe_6 = O_3 = Mo_2$, or, $Fe_3 = Mo$. This gives the ratio 167.52 Fe = 96 Mo, or, 1 Fe = 0.5732 Mo.

[3] When ferric phosphate is used, it is actually iron and not molybdenum that is titrated. The ferric salt does the oxidizing previous to the titration, and a corresponding amount of ferrous salt is formed; this is then titrated with permanganate.

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9. Gravimetric Determination as Lead Molybdate.—Proceed according to Method 1, up to the point where the molybdenum sulphide has been dissolved and filtered (4). The filtrate should, in this case, be received in a 400-cc. beaker instead of an 8-oz. flask. Make the liquid in the beaker alkaline with strong ammonia, adding about 10 cc. in excess, then reacidify with acetic acid in a few cubic centimeters excess. (Filter again if necessary, washing with hot water.)

Have ready a 4 per cent solution of lead acetate, made by dissolving 20 grams of the salt in 500 cc. of water and adding a few cubic centimeters of acetic acid to clear the liquid. One cubic centimeter of this solution will precipitate about 0.01 gram of molybdenum, or 2 per cent on the basis of 0.5 gram of ore taken.

Add an excess of this lead acetate to the molybdenum solution, heat to boiling and then allow the crystalline precipitate to settle, hot, for a short time. Filter while hot, through an ashless filter, and wash thoroughly (till free from chlorides) with hot water. Transfer

the moist filter and precipitate to a weighed porcelain crucible, heat gently until dry, then maintain at a dull-red heat for about twenty minutes. The paper will burn off without danger of reducing the lead. Cool and weigh as $PbMoO_4$. The weight of the latter, multiplied by 0.2615, will give the weight of the Mo.

None of the ordinary elements interfere.

10. Gravimetric Lead Molybdate Method. Bonardi's Modification.*—Bonardi states that this is undeniably one of the best methods for determining molybdenum.

Weigh 0.25 to 5.0 grams of the finely pulverized material (depending upon the grade of sample, not to contain over 0.15 gram of Mo, equivalent to 0.25 gram MoS_2) into a 250-cc. Erlenmeyer flask. Add 15 cc. of nitric acid and heat until the brown fumes are gone; then add 5 to 10 cc. of hydrochloric acid and heat about twenty minutes, or nearly to dryness. Allow to cool, wash down the sides of the flask with water, and heat about ten minutes longer to dissolve as much of the base metal salts as possible. For wulfenite ores, steels and alloy products it is best to add about 6 cc. of sulphuric acid just previous to this last heating and run down to fumes, again allowing to cool, washing down with water and then heating for about ten minutes.

Now make the mixture strongly ammoniacal, heat for a few minutes and filter hot, washing with hot water at least five times. Puncture the filter and wash the residue of insoluble material, iron and aluminum hydroxides into the original flask. Add sufficient hydrochloric acid to dissolve the precipitated hydroxides, then make the solution strongly ammoniacal, heat, filter and wash as before, receiving the filtrate in the beaker containing the first portion. This second precipitation is to recover any molybdenum occluded by the separated hydroxides. The molybdenum is now in the form of ammonium molybdate in a solution free from silica, iron and alumina, also lead if the sample was taken to fumes with sulphuric acid.

The volume of the solution should now be approximately 350 cc. Add a little methyl orange as indicator, make just acid with hydrochloric acid and then add about 5 cc. in excess. Add 5–10 grams of ammonium acetate and 2–5 cc. of acetic acid. Heat to boiling.

Have ready a lead acetate solution containing about 18 grams of the crystallized salt per liter. Run this slowly into the boiling-hot molybdenum solution from a burette, until a test drop taken from

* J. P. Bonardi, formerly of U. S. Bureau of Mines. Private communication.

the solution gives no color change on a spot plate with a drop of freshly made tannic acid solution (about 0.10 gram dissolved in 20 cc. of water). Now add 2–5 cc. excess of the lead acetate solution and 10 cc. of acetic acid. Heat to boiling and keep at the boiling-point from fifteen to thirty minutes, or until the precipitated $PbMoO_4$ has crystallized and settled.

When settled, filter while hot, and wash well with a hot 2 or 3 per cent solution of ammonium acetate. The initial washing may be with hot water, but water alone will eventually cause the precipitate to run through, by becoming colloidal. A bulky precipitate is best washed two or three times by decantation, with a dilute solution of ammonium nitrate, before it is transferred to the filter.

Place the washed filter and precipitate in a fire-clay annealing cup, and ignite at a dull-red heat, in a muffle or otherwise. Prolonged ignition at a much higher temperature than necessary to destroy the paper does no harm. After cooling the ignited precipitate, brush it out of the annealing cup into the balance pan, and weigh it. If it has been properly washed it will not adhere to the cup. It should be of a yellowish-white color.

The weight of the $PbMoO_4$, multiplied by 0.2615, will give the corresponding weight of molybdenum.

Note.—Phosphorus, arsenic and antimony might interfere with the above method by forming insoluble compounds with the various base metals in the acetic acid solution. With most ores there is usually sufficient iron present to combine with and remove these interfering elements in the ammonia precipitation. In unusual cases, or if in doubt, the addition of 2 grams of ferric chloride or sulphate, before the precipitation with ammonia, will ordinarily be sufficient to take care of all the arsenic, antimony and phosphorus. As a general rule, the iron required is at least ten times the weight of the arsenic and antimony assumed to be present. Soluble salts of mercury, copper, cadmium, zinc, nickel, cobalt and manganese do not interfere with the method. Vanadium and tungsten must be removed.

CHAPTER XXI

NICKEL AND COBALT

1. Nickel Alone. Method for Ores, etc.—Weigh 0.5 gram of the ore, and make the sulphate fusion, or melt, in an 8-oz. flask, as described in ANTIMONY, 2. To the cool residue add 100 cc. of water and 5 cc. of hydrochloric acid. Heat, or boil gently, to dissolve or disintegrate the cake. See that all anhydrous ferric sulphate goes into solution. It usually appears in the agitated liquid as pearly scales which gradually disappear. Without cooling, pass in hydrogen sulphide for about ten minutes. Filter through a 9-cm. filter from the sulphides of arsenic, antimony, copper, etc., washing with hydrogen sulphide water. Receive the filtrate in a beaker.

2. Boil the filtrate until the hydrogen sulphide is expelled, then add a little bromine water to oxidize the iron and boil off the excess. Now add 2 grams of tartaric acid (to keep iron in solution) and 2 grams of ammonium chloride (to keep manganese and zinc in solution). Make slightly alkaline with ammonia. If a cloud forms, add more ammonium chloride until clear. See that the liquid remains slightly alkaline.

3. Heat nearly to boiling. Add dimethyl glyoxime in 1 per cent alcoholic solution, until the weight of the reagent added is about seven times the assumed weight of the nickel present. Add ammonia, if necessary, until a faint but distinct odor is apparent. Stir well, and then set the beaker in a hot place for about fifteen minutes. Filter the hot mixture through a weighed Gooch crucible, and wash well with hot water.

4. Dry in an oven at 110–120° C. to constant weight. The scarlet-red nickel compound is nickel-dimethyl glyoxime. It has the formula $(C_4H_7N_2O_2)_2Ni$ and contains 20.32 per cent of nickel.[1]

5. Cobalt does not interfere unless it is present in considerable amount. If more than 0.1 gram is present, a large excess of ammonia

and dimethyl glyoxime is necessary to keep it in solution; hence it is better in such a case to start with less than 0.5 gram of material.

Theoretically, about 4 parts of dimethyl glyoxime are required for 1 part of nickel,[2] but an excess is always advisable. An excess does no harm unless the alcohol of the reagent solution exceeds more than one-half the volume of the aqueous nickel solution, in which case the alcohol has a slight solvent action on the precipitate.

6. On the basis of 0.5 gram of ore taken for analysis, and using 7 parts of the reagent in 1 per cent alcoholic solution to 1 part of nickel, for every per cent of nickel assumed to be present, add 3.5 cc. of the dimethyl glyoxime solution.

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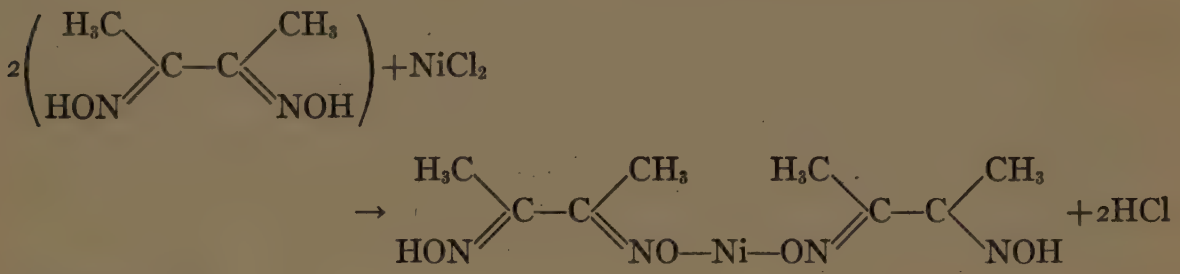
[1] The formula of nickel-dimethyl glyoxime being $(C_4H_7N_2O_2)_2Ni$, the molecular weight is 288.864. The atomic weight of nickel is 58.68, therefore the percentage of nickel in the compound is $58.68/288.864 \times 100 = 20.32$.

[2] The reaction between nickel and dimethyl glyoxime may be represented as follows:



or, more briefly,

$$(C_4N_2O_2H_8)_2 + NiCl_2 \rightarrow (C_4N_2O_2H_7)_2Ni + 2HCl.$$

The molecular weight of dimethyl glyoxime is 116.1. This doubled, or 232.2, = 58.68 Ni. Thus 1 part by weight of nickel requires theoretically 3.958 parts of dimethyl glyoxime, or, roughly, 4 parts.

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7. Cobalt. Method for Ores, etc.*—Treat 0.5 gram of the ore precisely as described in **1**. Having the filtrate from the hydrogen sulphide precipitation in a sufficiently large beaker, boil off the excess of hydrogen sulphide. Remove from the heat, and with the beaker covered to avoid loss by effervescence, add sodium carbonate until the solution is plainly alkaline, then reacidify slightly with hydrochloric acid. Heat to boiling and boil a short time, to expel carbon dioxide and thus avoid subsequent spattering. Remove the beaker cover and

* Modified from Giles' description. W. W. Scott's Standard Methods of Chemical Analysis.

add an emulsion of zinc oxide to the hot solution in evident excess, as shown by the presence of undissolved zinc oxide after boiling. Filter, while hot, through an 11-cm. filter and wash ten times with hot water. Receive the filtrate in a large beaker.

8. Dilute to about 300 cc. with hot water. Add 6 cc. of strong hydrochloric acid and heat to boiling. Now, for every per cent of cobalt presumed to be present, add 1 cc. of a freshly prepared solution of nitroso-beta-naphthol. This solution is made by dissolving 1 gram of the salt in 10 cc. of glacial acetic acid. After adding the reagent, boil for about two minutes, then remove from the heat, stir well and set aside for a short time until the bright red precipitate settles.

9. Filter the hot solution through a filter of convenient size. Rinse out the beaker with hot 1 : 1 hydrochloric acid, then wash the filter and precipitate five times with this acid, alternating with five washes with hot water. Finally wash ten times with hot water.

10. Transfer filter and precipitate to a weighed quartz or porcelain crucible, ignite gently until the carbonaceous matter is burned off, and then at as high a temperature as possible to constant weight. Weigh the residue as Co_3O_4. This weight, multiplied by 0.7343, will give the weight of the cobalt.[1]

If desired, the Co_3O_4 may be reduced in hydrogen and weighed as metal.

11. The nitroso-beta-naphthol precipitate is voluminous, and therefore the quantity of sample taken for analysis should not contain over 0.1 gram of cobalt, or 20 per cent on the basis of 0.5 gram taken. None of the ordinary elements interfere with the method as described. The method is especially suitable for the determination of cobalt in the presence of comparatively large amounts of nickel. Nitroso-beta-naphthol, $C_{10}H_6O(NOH)$, forms with cobalt the compound $Co(C_{10}H_6O(NO))_3$, cobalti-nitroso-beta-naphthol, which is insoluble in hydrochloric acid, while the corresponding nickel compound is soluble.

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[1] The molecular weight of Co_3O_4 is 240.91. This corresponds to three times the atomic weight of cobalt, or, three times $58.97 = 176.91$. Then, $176.91/240.91 = 0.7343$, the factor required.

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12. Electrolytic Method, Giving Combined Nickel and Cobalt.—Decompose 0.5 gram of the ore, as completely as possible, in a covered

evaporating dish, by heating with 10 cc. of hydrochloric acid and 5 cc. of nitric acid. Boil to small bulk, then add 10 cc. of hydrochloric acid and 5 grams of pure, finely crystallized ammonium chloride. Remove the cover and evaporate on a water-bath, to complete dryness. Allow to cool, add 25 cc. of strong ammonia, and warm on the water-bath, with frequent stirring, using a rubber-tipped glass rod, until the disintegration of the residue is complete. Filter into a beaker, through a 9-cm. filter, and wash ten times with warm dilute ammonia. The residue on the filter will be free from all but negligible traces of nickel or cobalt.

13. Again evaporate on the water-bath to small bulk, and then transfer the solution to a $2\frac{1}{2}$-in. evaporating dish, removing any residue adhering to the large dish with a few drops of hydrochloric acid, and adding to the rest. Continue the evaporation on the water-bath to complete dryness, then heat carefully over a small free flame until all the ammonium chloride present is expelled. Any zinc present will be driven off at the same time.

14. When cool, dissolve the residue in nitrohydrochloric acid and expel the excess of acid by evaporating nearly to dryness. Take up in 5 cc. of hydrochloric acid, transfer to a beaker, dilute to about 250 cc. with hot water, and pass in hydrogen sulphide until cold. Filter off any precipitated sulphides, washing with dilute hydrogen sulphide water. Receive the filtrate in a large beaker.

Boil the solution to sufficiently small bulk and then transfer to an evaporating dish and evaporate on a water-bath to complete dryness. Dissolve the residue in a little dilute sulphuric acid. Transfer to the beaker in which the electrolysis is to be made, add about 5 grams of ammonium sulphate and 40–60 cc. of strong ammonia, and dilute to about 125 cc. with distilled water. The solution is now ready for electrolysis.

The electrolytic apparatus may be the same as described for copper (see COPPER, 18). The beaker used is about 5 cm. in diameter and 8–9 cm. high. See article, ELECTROLYSIS, for details as to arrangement of apparatus, etc.

15. Insert the electrodes and electrolyze at room temperature with a current density of $ND_{100} = 0.5 - 0.7$ amp. and an electrode tension of 2.8–3.3 volts. The electrolysis is usually finished in three to four hours. To test for its completion, a little of the solution may be removed with a capillary tube and tested with ammonium sulphide.

If no black precipitate is obtained, the operation may be considered ended. The solution should still be strongly ammoniacal. Having broken the circuit, remove the cathode, wash it first with water and then with alcohol (preferably absolute), dry at about 100° C., and weigh. The excess over the original weight represents the combined nickel and cobalt.

16. Separation of Nickel and Cobalt.—Perhaps the best method of accomplishing this is to determine the two metals together electrolytically, as just described, and then determine one of them separately, thus arriving at the other by difference.

Dissolve the metals from the electrode by boiling for about twenty minutes with strong nitric acid in a covered beaker. Remove and wash the electrode, and evaporate the solution to small bulk, to remove most of the acid. Ordinarily, this is best done in an evaporating dish on a water-bath. Transfer the concentrated solution to a beaker, add about 2 grams of ammonium chloride and then make very slightly alkaline with ammonia. Dilute to about 150 cc. and determine the nickel according to **3–4.**

If preferred for any reason, the cobalt may be determined instead of the nickel. In this case the concentrated solution in the evaporating dish should have an excess of hydrochloric acid added to it and be evaporated to complete dryness, to expel nitric acid. Take up the residue in 6 cc. of hydrochloric acid and a little water, dilute to about 300 cc. with hot water and continue according to **8**, *et seq.*

Of course, either the nickel or the cobalt may be determined in the original ore, according to the previous methods, before the electrolysis is finished.

17. Separation of Nickel and Cobalt by Liebig's Potassium Cyanide Method.—Proceed as described in **12**, **13** and **14** until zinc, if present, has been expelled and the nitrohydrochloric acid solution of the residue has been evaporated nearly to dryness to expel the excess of acid. Now dilute sufficiently and neutralize with pure potassium hydroxide, finally adding 5 grams in excess; then add pure potassium cyanide until the precipitate redissolves and the potassium cyanide is in slight excess. To the warm solution add saturated bromine water with constant stirring, until the precipitation of the nickel as black nickelic hydroxide is complete. The solution must be kept strongly alkaline throughout the process. Finally, dilute the mixture with cold water and filter, washing the precipitate with hot water.

Dissolve the precipitate in dilute sulphuric acid and determine the nickel electrolytically, as described in 14, at same point.

The filtrate contains the cobalt as potassium cobalticyanide. Acidify with dilute sulphuric acid and evaporate as far as possible on the water-bath, then add a little concentrated sulphuric acid and heat the mixture over a free flame until dense white fumes are evolved and effervescence has ceased. The cobalt in the colorless potassium cobalticyanide is thus changed into the rose-red sulphate. Cool, dilute, filter from any silica, and determine the cobalt in the filtrate electrolytically, precisely as described for nickel (14, at same point). Or, the filtrate may be treated as follows: Heat to boiling in a porcelain casserole and precipitate the cobalt as black cobaltic hydroxide by the addition of potassium hydroxide and bromine water. Filter through a close filter (such as Schleicher and Schull's No. 589, blue band), dry and ignite. After cooling, extract with water to remove the small amount of alkali always present, then dry the residue and ignite in a current of hydrogen in a Rose crucible, finally weighing the cobalt as metal.

After weighing, dissolve the metal in hydrochloric acid, evaporate to dryness, moisten the residue with hydrochloric acid, dilute and filter off the small residue of silica. Ignite, weigh and deduct this weight from the previous one to obtain the true weight of the cobalt.

18. Sensitive Test for Nickel.*—α-dimethyl glyoxime is a very sensitive reagent for nickel in solution, and gives a scarlet precipitate, or, with traces of nickel, a yellowish solution from which the red precipitate separates on cooling. The best method of applying this reagent is to remove the excess of acid from the solution to be tested, by adding excess of ammonia or sodium acetate, and then to add the powdered dimethyl glyoxime, and to boil for a short time. Distinct indications are obtained with solutions containing only 1 part of nickel per 400,000 of water. The reaction is not disturbed by the presence of ten times as much cobalt as nickel, but when the proportion of cobalt is much greater than that of nickel, it is best to add a very large excess of ammonia to the liquid and to shake repeatedly, excess of the dimethyl glyoxime being then added and the solution boiled for a short time. In testing by this method for nickel, in such products as commercial cobalt salts, the reaction is manifested by the appearance of a scarlet scum rising up the walls of the test-tube, but it is generally

* L. Tschugaeff. Ber., 1905, 38, 2520–2522. Jour. Soc. Chem. Ind., XXIV, 941.

necessary to filter or siphon off the cooling liquid and wash the residue with water; in the presence of nickel this residue is red, but if nickel is absent, it is quite colorless. In this way 1 part of nickel can be detected when admixed with 5000 parts of cobalt.

19. Sensitive Test for Cobalt.*—If a concentrated solution of ammonium thiocyanate is added to a cobaltous solution, the latter becomes a beautiful blue, owing to the formation of ammonium cobaltous thiocyanate. On the addition of water the blue color disappears and the pink color of the cobaltous salt takes its place. If, now, amyl alcohol is added (or a mixture of equal parts of amyl alcohol and ether), and the solution is shaken, the upper alcoholic layer is colored blue. This reaction is so sensitive that the blue color is recognizable when the solution contains only 0.02 mg. of cobalt. Nickel salts produce no coloration of the amyl alcohol. If, however, iron is present, the red $Fe(CNS)_3$ is formed, which likewise colors the amyl alcohol, making the blue color (due to cobalt) very indistinct, so that under some conditions, it can no longer be detected. However, if some sodium carbonate solution is added, the iron will be precipitated as ferric hydroxide, while the blue color produced by the cobalt is unaffected.

20. Determination of Nickel in Steel.†—Dissolve about 0.5 gram of the steel in 10 cc. of strong hydrochloric acid, add sufficient nitric acid to completely oxidize the iron, and, if silica separates, add also a little hydrofluoric acid. Finally, add 2 or 3 grams of tartaric acid and dilute the solution to about 300 cc. Carefully test the solution to see if enough tartaric acid is present to prevent any precipitation of iron when the solution is made alkaline with ammonia, and add more tartaric acid if necessary. Now neutralize the solution so as to leave it *slightly* acid, heat nearly to boiling and add 20 cc. of a 1 per cent alcoholic solution of dimethyl gloxime; then very carefully neutralize the slight excess of acid with ammonia leaving the solution so that it barely smells of this reagent. Filter the hot mixture through a Gooch filter, wash the precipitate with hot water and dry at 110°–120° C. for forty-five minutes. Weigh as $Ni(C_4H_7N_2O_2)_2$, containing 20.32 per cent of nickel.

The determination can be made within about two hours. The

* Vogel's reaction. From Treadwell's Analytical Chemistry (Hall), Vol. I, p. 137.

† Treadwell's Anal. Chem. (Hall), 2nd Ed., Vol. II, p. 146. O. Brunck, Stahl und Eisen, 28, 331.

results are accurate, but may sometimes appear low, from the fact that any cobalt present is not determined with the nickel, as it may be with some other methods.

21. Volumetric Method for Nickel.—In the following method * nickel may be accurately determined in the presence of aluminum, ferric iron, magnesium and zinc. Manganese and copper must be removed. Cobalt counts as nickel. If present, it may be detected during the titration by the darkening of the solution. The method is especially applicable to the assay of nickel mattes and German silver. In the case of ores it may be applied to the purified solution after removing iron, manganese, copper, etc., and boiling off any hydrogen sulphide.

The following solutions are required:

Standard silver nitrate, containing about 3 grams of silver per liter. The strength of this solution must be accurately known.

Potassium iodide, 10 per cent solution.

Potassium cyanide, 22 to 25 grams per liter. This solution must be tested every few days.†

Standardizing the Cyanide Solution.—First, accurately establish the relation of the cyanide to the silver solution. Run into a beaker 3 or 4 cc. of the former, dilute this with about 150 cc. of water, render slightly alkaline with ammonia, and then add a few drops of the potassium iodide. Now carefully run in the silver solution until a faint permanent opalescence is produced which is finally caused to disappear by the further addition of a mere trace of cyanide. The respective volumes of the silver and cyanide solutions are then read off, and the equivalent in cyanide of 1 cc. of silver solution calculated. Now calculate the metallic silver value of 1 cc. of the cyanide solution and multiply this by 0.2720 to obtain the nickel value.

22. *Titration of a Nickel Solution.*—The nickel solution (containing not more than about 0.1 gram of nickel) must have sufficient free acid present to prevent the formation of any precipitate on the subsequent addition of ammonia to alkaline reaction; if this is not the case, a little ammonium chloride may be added. Make distinctly alkaline with ammonia, add a few drops of the potassium iodide solution and dilute to 150 or 200 cc. A few drops of the silver solution are now run

* T. Moore, Chem. News, 72, 92.

† The addition of about 5 grams of potassium hydroxide per liter is said to increase its permanency.

in and the solution stirred to produce a uniform turbidity. Cool the mixture to at least 20° C. and it is ready to be titrated with the potassium cyanide solution, which is added slowly and with constant stirring until the precipitate wholly disappears; a few extra drops are added, after which the beaker is placed under the silver nitrate burette, and this solution gently dropped in until a faint permanent turbidity is again visible; this is now finally caused to dissolve by the mere fraction of a drop of the cyanide. A correction must now be applied for the excess of cyanide added, by noting the amount of silver solution employed and deducting its value in cyanide solution from the amount of the latter used. The amount of cyanide solution actually consumed by the nickel is thus arrived at, from which the percentage of nickel is calculated.

If aluminum, magnesium or ferric iron are present, they may be kept in solution with either citric acid, tartaric acid or sodium pyrophosphate. In the presence of zinc, use sodium pyrophosphate. The action of iron is somewhat deceptive, as the solution, once cleared up, often becomes troubled again on standing for a minute; should this occur, a further addition of cyanide must be given until the liquid is rendered perfectly limpid. The temperature of the solution should never exceed 20° C.: above this the results become irregular. The amount of free ammonia also has a disturbing influence; a large excess hinders or entirely prevents the reaction; the liquid should, therefore, be only slightly but very distinctly alkaline. The potassium cyanide should be as pure as possible. The most hurtful impurity is sulphur, which causes a darkening of the solution owing to the formation of the less readily soluble silver sulphide. To get rid of the sulphur impurity it is necessary to thoroughly agitate the cyanide liquor with lead oxide, or, what is far preferable, bismuth oxide.

In the hands of Mr. Moore, the above method, after many thousands of determinations, has been found to be more accurate and reliable than either the electrolytic or gravimetric methods.

23. Modification of the above Method Applied to the Determination of Nickel in Nickel Steel.*—The determination can be made with speed and accuracy, even in the presence of iron, manganese, chromium, zinc, vanadium, molybdenum and tungsten.

Requirements.—The potassium cyanide solution should be about equivalent to a tenth-normal silver solution, and is prepared by dis-

* Treadwell's Anal. Chem. (Hall), 2d Ed., p. 656. Numerous references are given.

solving 13.5 grams of pure potassium cyanide and 5 grams of potassium hydroxide in water and diluting to 1 liter.

The silver nitrate solution is made exactly tenth-normal and is prepared by dissolving 8.4944 grams of $AgNO_3$ in water and diluting to exactly 500 cc. One cubic centimeter of this solution is equivalent to 0.01302 gram KCN, or to 0.002935 gram Ni. It is used for standardizing the potassium cyanide solution, and in the analysis itself.

The potassium iodide solution contains 2 grams KI in 100 cc.

Determination.—Dissolve 1 gram of the steel in a casserole with 10 to 15 cc. of nitric acid (sp. gr. 1.20), adding a little hydrochloric acid if necessary. After the steel has dissolved, add 6 to 8 cc. of sulphuric acid (1 : 1) and evaporate until fumes of the latter begin to come off. Cool the residue, add 30 to 50 cc. of water, and heat until the anhydrous ferric sulphate has all dissolved. Transfer the solution to a 400-cc. beaker, filtering if necessary, and add 13 grams of sodium pyrophosphate dissolved in 60 cc. of water at about 60° C. The pyrophosphate solution must not be boiled, as this causes the formation of normal phosphate. The addition of the sodium pyrophosphate produces a heavy white precipitate of ferric pyrophosphate. Cool the liquid to room temperature and add dilute ammonia (1 : 1), drop by drop, while stirring constantly, until the greater part of the precipitate has dissolved and the solution has assumed a greenish tinge. At this point it should react alkaline toward litmus, but should not smell of free ammonia. Now heat the solution gently, while stirring, and the remainder of the pyrophosphate will dissolve, giving a perfectly clear light-green solution. If the ammonia is added too fast, or the solution is not carefully stirred, a brownish color is likely to result, but this can usually be overcome by carefully adding a few drops of dilute sulphuric acid. Cool the clear solution to room temperature and add 5 cc. of the standard silver nitrate solution together with 5 cc. of the potassium iodide. Now titrate the solution with the potassium cyanide, adding it until the precipitate of silver iodide has disappeared. Finish the titration by adding just enough additional silver nitrate to again produce a slight turbidity. Before calculating the percentage of nickel, make a correction for the amount of silver nitrate added.

Remarks.—The results obtained by the potassium cyanide titration of nickel are said to be very satisfactory. It can be carried out in the presence of most of the other elements of the ammonium sulphide

group.* If copper is present in amounts not exceeding 0.4 per cent, the copper will replace almost exactly three-quarters of its weight of nickel. In case chromium is present, the dark color due to the presence of chromic salts may be obviated by adding to the original sulphuric acid solution a 2 per cent solution of potassium permanganate until a slight permanent precipitate of manganese dioxide is obtained, whereby the chromium is oxidized to chromic acid. The solution is filtered, concentrated in a 400-cc. beaker to about 60 cc., then treated with sodium pyrophosphate, as described above. The method is not applicable in the presence of cobalt, but when the amount of the latter does not exceed one-tenth the amount of nickel present, the titration can be carried out successfully and the results represent the amount of nickel and cobalt present.

24. Volumetric Method for Nickel in Ores.†—This is a modification of the cyanide method described in **21**. The following description is given in the words of its author. Two standard solutions are required; silver nitrate and potassium cyanide.

The standard silver nitrate solution is made by dissolving 14.48 grams of C. P. recrystallized silver nitrate in distilled water and making up to 1000 cc. This solution should be made exact; if this is done, 1 cc. will be equivalent to 0.0025 gram of nickel. If the silver nitrate used is pure, and the resultant solution perfectly clear, there will be little need of standardization, as the methods most used in standardizing silver solutions will show a greater error than will be noted in the making up of the solution.

The standard cyanide solution should be made so as to be exactly equal in strength to the silver nitrate solution. This may be done as follows: Weigh up 12 grams of 95 per cent potassium cyanide, or, 11.6 grams of 99 per cent, dissolve in water and dilute to 1000 cc. Fill one burette with this solution and another with the silver nitrate solution. Run 50 cc. of the cyanide solution into a large beaker, add 10 drops of a 5 per cent solution of potassium iodide, 10 cc. of ammonia, dilute to about 200 cc. and titrate with the silver nitrate solution until a distinct, but not too deep, yellowish cloud of silver iodide is formed, indicating that the end-point has been reached. The cyanide will be found to be slightly stronger than the silver nitrate. For

* Instead of using sodium pyrophosphate to prevent the interference of iron and other metals, many chemists use citric or tartaric acid.

† E. C. D. Marriage, Eng. and Min. Jour., July, 1921, 174.

example: 51.3 cc. of the silver nitrate solution may have been required to neutralize 50 cc. of the cyanide solution, in which case add 1.3 cc. of water to each remaining 50 cc. of the cyanide. Another trial should demonstrate the two solutions to be of equal strength.

25. Treatment of an Ore.—Weigh 0.5 gram of the ore into an 8-oz. flask, add 15 cc. of nitric acid, heat till red fumes have ceased to come off, add 5 grams of potassium chlorate and take to complete dryness, but avoid baking. When cool, add 10 cc. of hydrochloric acid and take to dryness as before. Allow to cool and take up with 10 cc. of hydrochloric acid and 40 cc. of water. Heat gently until all soluble matter has gone into solution, filter, washing thoroughly with successive small amounts of hot water. Make the filtrate alkaline with ammonia, add 10 cc. of bromine water and boil off the excess of bromine. Filter, redissolve the residue with hydrochloric acid and reprecipitate to recover any occluded values. Filter through the same filter as before. Acidify the filtrate with hydrochloric acid and add 10 cc. in excess. If manganese is known to be absent, the ammonia precipitation should be omitted, in which case the filtrate from the flask is ready for the next step. In either case, hydrogen sulphide is passed through the hydrochloric acid solution until no further precipitation takes place. Filter, wash thoroughly with hot water, and boil off the excess of hydrogen sulphide from the filtrate. If the solution exceeds 150 cc. in volume, reduce by evaporation. Add 15 cc. of bromine water, to oxidize the solution thoroughly, and boil off the excess of bromine. Cool to approximately 60° F., add 15 cc. of a 10 per cent solution of citric acid, then neutralize with ammonia and add 10 cc. in excess. If there is any nickel present the solution will have a distinct blue color, nickel being similar to copper in this respect. The solution is now ready for titration and should be about 200 cc. in volume.

26. Titrate with the standard cyanide solution until the blue color has disappeared, and add 5 to 10 cc. in excess. It is well to add a round number of cubic centimeters in order that the calculation may be simplified. Add about 10 drops of the potassium iodide indicator and titrate with the silver nitrate solution until the yellowish cloud appears. If there is any doubt as to the correctness of the end-point, add an additional 5 cc. of the cyanide and again finish with the silver nitrate. The results should correspond; that is, if 30 cc. of the cyanide solution had been used and the silver nitrate burette showed a

reading of 20 cc., then, if the titration is correct, 35 cc. of the cyanide should take 25 cc. of the silver nitrate, the difference in both cases being 10 cc. It is this difference between the readings of the two burettes that measures the quantity of nickel present, each cubic centimeter of the difference being equivalent to 0.0025 gram of nickel. In the example quoted, the difference is 10 cc., which is equivalent to 5 per cent of nickel, the weight of the ore taken being 0.5 gram.

If the cyanide solution is not exactly equal in strength to the silver nitrate solution, the quantity of cyanide used must be calculated to its equivalent in silver nitrate before subtraction is made.

There are few elements that interfere in this determination, manganese, copper, lead, silver, arsenic and antimony being eliminated in the two precipitations described. Cobalt, when present, counts as so much nickel. Zinc, when present in any quantity, seems to have no effect whatever.

Note.—In view of the fact that there is considerable difficulty in making the cyanide solution exactly equal to the silver solution, and, furthermore, as it is unstable and will not hold its strength very long, it would seem that the employment of an approximately correct solution, standardized whenever considered necessary and used with a factor to show its equivalent in correct solution, would ordinarily be the most convenient plan. (A. H. L.)

27. Electrolytic Method in General Use at Cobalt, Ont., Canada.*—Treat 1 gram of the ore in a 250-cc. beaker with 10 cc. of strong nitric acid and 5 cc. of strong hydrochloric acid. When decomposition is complete add 15 cc. of strong sulphuric acid and boil until the sulphuric acid is fuming strongly. Allow to cool, take up with water, add 5 cc. of strong hydrochloric acid to assist solution, and boil gently for a few minutes. Remove from the heat and pass hydrogen sulphide through the hot solution for ten to fifteen minutes, then heat again and once more pass in hydrogen sulphide until all the arsenic is precipitated and the supernatant liquid is clear. Filter, washing the precipitate six or seven times with hot water. Boil the filtrate to expel the hydrogen sulphide and reduce to a volume of about 150 cc. Filter and wash as before. Heat the filtrate to boiling and add 15 to 20 cc. of hydrogen peroxide to effect oxidation. After boiling a short time, remove from the heat and allow to cool somewhat and then separate the iron as basic acetate as follows: Make the solution just

* Communicated by Mr. B. C. Lamble, chemist at the La Rose Mines, Ltd., Cobalt.

alkaline with ammonia and then reacidify slightly with hydrochloric acid. Add 15 grams of solid sodium acetate (crystals) and boil. Filter off the iron precipitate, washing with hot water, and place the filtrate over the heat to concentrate. Dissolve the precipitate in hot dilute hydrochloric acid, dilute to about 150 cc. and repeat the precipitation as just described. Unite the two filtrates, boil down to about 100 cc. and filter. Make the filtrate alkaline with ammonia and add about 20 cc. in excess. Electrolyze the hot solution (which should have a volume of 125 to 130 cc.), keeping it hot and highly ammoniacal during the electrolysis. (See **12**.) A gauze cathode is preferred. When the operation is apparently finished (in $2\frac{1}{2}$ to $3\frac{1}{2}$ hours), test for nickel and cobalt on a spot-plate with ammonium sulphide. Wash the cathode first with water, then with alcohol, dry at about 100° C., and weigh. This gives the combined nickel and cobalt.

Dissolve the deposit in a 250-cc. beaker in strong nitric acid and wash off the cathode with hot water. Boil or evaporate the solution to a syrup. Add about 20 cc. of water and then add a solution of potassium hydroxide until a precipitate of cobalt hydroxide (blue) remains undissolved. Now acidify with acetic acid and add a few cubic centimeters in excess; then add about 25 grams of potassium nitrite and stir until dissolved. Boil gently for about twenty minutes, then dilute with water until the beaker is about five-sixths full and allow to stand overnight. Decant and filter the cobalt precipitate and wash it a few times with ice-cold water, or water containing about 5 per cent of potassium nitrite and barely acidified with acetic acid. Dissolve the precipitate in hot dilute sulphuric acid and boil down the solution until the sulphuric acid is fuming. Cool, dilute with water, heat to boiling and filter. Make the filtrate alkaline with ammonia, having about 20 cc. in excess, dilute to about 125 cc. and electrolyze as described above. This gives the cobalt, and the nickel is determined by the difference between this weight and that of the combined nickel and cobalt.

Note.—I would recommend an 8-oz. flask instead of a beaker for the decomposition, and 7 cc. of sulphuric acid instead of 15 cc. Any globules of separated sulphur may be completely volatilized by allowing the sulphuric acid to boil very gently for some time after coming to fumes. In case an ore contains much arsenic or antimony, it would seem to be an advantage to employ the method of decomposition described in Antimony 2. (A. H. L.)

CHAPTER XXII

PHOSPHORUS

1. Gravimetric Method for Iron Ores.*—Take 1.63 grams of the finely ground ore. Dissolve by boiling gently for twenty minutes with 40 cc. of strong hydrochloric acid (1.20 sp. gr.) in a covered 8-oz. beaker. Dilute with 20 cc. of water, and filter, washing with water. Receive the filtrate in an 8-oz. beaker. Evaporate the filtrate to dryness on a sand-bath or hot plate. While the filtrate is evaporating ignite the filter and insoluble residue in a platinum crucible. After the paper is burned off, break up any lumps with a platinum rod and then ignite again at a red heat for about two minutes. Cool, and transfer the ignited residue to the beaker in which the filtrate is evaporating. Any phosphorus that may have remained with the insoluble residue is thus rendered soluble by the ignition and recovered.† After evaporation, add to the residue in the beaker 25 cc. of strong nitric acid (sp. gr. 1.42), cover the beaker and boil to about 12 cc. Now dilute with 12 cc. of water and filter, washing with water. Receive the filtrate in an 8-oz. flask. The total bulk should not exceed 50 cc. Heat to 40°–45° C., add 60 cc. of molybdate solution,‡ previously filtered and heated to 40°–45° C., stopper the flask and shake for five minutes. Allow to stand in a warm place for fifteen minutes and then filter through a Gooch crucible that has been previously dried at 110° C., and weighed. Wash with a 2 per cent nitric acid solution till free from iron, and then twice with 95 per cent alcohol. Dry twenty minutes at 110° C. and weigh. The dried residue contains 1.63 per cent of phosphorus; therefore each milligram found corresponds to 0.001 per cent of phosphorus in the ore.

2. Error Caused when Titanium is Present.—Blair § notes the fact that if a solution of ferric chloride containing titanic and phos-

* Mainly the method of John S. Unger, Trans. Engineers Soc. of Western Penn., 1896.

† Mixer and Dubois. Jour. Am. Chem. Soc., XIX, p. 614.

‡ See below, 7.

§ Chem. Anal. of Iron, 3d Ed., p. 86.

phoric acids is evaporated to dryness, a compound of TiO_2, P_2O_5, and Fe_2O_3 is formed, which is completely insoluble in hydrochloric acid (and presumably in nitric acid also). When titanium is present in the material analyzed and such a residue is obtained on filtering the nitric acid solution after evaporation to dryness, it may be treated as follows:

3. Dry the residue and burn off the filter paper by ignition in a platinum crucible. Moisten the cool residue with a few drops of strong sulphuric acid and add sufficient hydrofluoric acid to dissolve the silica. Evaporate cautiously and heat until all the sulphuric acid is driven off. Cool, add 2 or 3 grams of sodium carbonate and fuse the mixture. Dissolve the melt in hot water, filter and wash. Receive the filtrate in a 6-oz. flask and acidify with nitric acid. The total bulk should not exceed 50 cc. Heat to 40°–45° C., add 25 cc. of molybdate solution, previously filtered and heated to the same temperature, and finish as described above for the main solution. The same filter, if desired, may be used for both filtrations of the yellow precipitate.

4. The presence of a large amount of titanium in an ore may be recognized by the peculiar milky appearance of the solution when it is diluted, before the insoluble matter is filtered off, and by the tendency of the latter to run through the filter when washed with water. In cases of uncertainty it is best to assume that titanium is present and proceed with the residue as described above. If the residue left after filtering the aqueous solution of the melt of 3 be dissolved in dilute hydrochloric acid, the solution placed in a test-tube and metallic zinc added, the liquid will first become colorless, from the reduction of the ferric iron, then, if titanium be present, pink or purple and finally blue, from the formation of Ti_2O_3.

5. **Method for Steel.**—Dissolve 1.63 grams of the steel, in a 6-oz. Erlenmeyer flask, in 30 cc. of nitric acid of about 1.20 sp. gr. Evaporate by boiling over a naked flame to 15 cc., add to the boiling solution 20 cc. of chromic acid solution (see 8 below) and again evaporate to 18 cc. Remove from the heat and wash down the sides of the flask with 5–7 cc. of water, and cool to 40°–45° C. Proceed from this point as directed above for ores (1). As in the case of ores, each milligram of yellow precipitate found corresponds to 0.001 per cent of phosphorus in the steel.

6. **Method for Pig Iron.**—Dissolve 1.63 grams, in a $4\frac{1}{2}$-inch covered evaporating-dish, in 40 cc. of strong nitric acid (sp. gr. 1.42). When

action has ceased, remove the cover and evaporate to dryness on a sand-bath. Place the dish and dry residue over a burner and heat cautiously with the naked flame until the mass ceases to evolve red fumes. Allow to cool, add 25 cc. of strong hydrochloric acid (sp. gr. 1.20), cover with a watch-glass and boil to 10 cc. Add cautiously 25 cc. of strong nitric acid (sp. gr. 1.42) and boil to 12 cc. Remove from the heat, rinse off the watch-glass and wash down the sides of the dish, using about 12 cc. of water, and then filter through an 11-cm. filter into an 8-oz. flask, washing with water. The solution should not exceed 50 cc. in bulk. Heat to 40°–45° C. and finish as described above for ores (1). Each milligram of yellow precipitate found corresponds to 0.001 per cent of phosphorus in the pig iron.

7. Molybdic Acid Solution.*—Mix 100 grams of molybdic acid to a paste, with 265 cc. of water. Add 155 cc. of strong ammonia water (sp. gr. 0.90) and stir until all is dissolved. To this solution add 66 cc. of strong nitric acid (sp. gr. 1.42), stir well and then set aside for an hour. In another vessel make a mixture of 395 cc. of strong nitric acid and 1100 cc. of water. Finally, pour the first solution into the second, stirring constantly. Allow to stand for twenty-four hours before using.

8. Chromic Acid Solution.—Dissolve 30 grams of pure chromic acid in 2 liters of strong nitric acid (sp. gr. 1.42), warming gently. This solution must be made up fresh at least every two weeks.

9. Volumetric Method for Iron Ores, Steel, etc.—Start with 2 grams of material and, according to its nature, proceed by one of the above-described methods until the yellow precipitate is finally obtained on the filter, which need not be weighed. Wash with a solution of acid ammonium sulphate, prepared by adding 15 cc. of strong ammonia (sp. gr. 0.90) and 25 cc. of strong sulphuric acid (sp. gr. 1.84) to 1 liter of water. Wash until 2 or 3 cc. of the wash-water give no brown reaction for molybdenum when tested with a drop of ammonium sulphide. Place the flask in which the precipitation was made under the funnel, and dissolve the ammonium phosphomolybdate on the filter by pouring over it a warm mixture of 5 cc. of strong ammonia water and 20 cc. of water. Wash the filter well with water.

10. Dilute the filtrate to about 100 cc. with cold water, and add 10 cc. of strong sulphuric acid. See that the temperature is 50–75° C., and the hot solution is ready for reduction, in accordance with the

* See **12.**

directions given in MOLYBDENUM, 4, which are to be followed to the end.

The Fe value of the permanganate solution multiplied by 0.01545 will give the P value.

This may be determined as follows:

11. When molybdic acid, Mo_2O_6, is reduced to Mo_2O_3, the latter requires the same amount of oxygen for reoxidation as is required to oxidize 6FeO to the ferric state. Therefore, 3Fe (ferrous) are equivalent to MoO_3, or 167.52 parts by weight of Fe are equivalent to 144 parts of MoO_3. Accordingly, the Fe factor of the permanganate, multiplied by 0.8598, will give the MoO_3 factor. Now, the formula of the ammonium phosphomolybdate is $(NH_4)_3 12MoO_3.PO_4$, therefore 1728 parts by weight of MoO_3 correspond to 31.04 parts of P, or, 1 part of $MoO_3 = 0.01797$ part of P. Thus by multiplying the Fe factor of the permanganate by 0.8598, and the product by 0.01797, the P factor is obtained, or, the Fe factor multiplied by 0.01545 gives the P factor.

12. **Note Regarding Molybdic Acid.**—The substance sold as molybdic acid frequently consists to a greater or less extent of alkali molybdate. Such material may be used for phosphorus determinations with fairly good results if the percentage of molybdic acid is determined, and the amount of substance taken in making up the molybdate solution regulated accordingly, so that the full quantity of molybdic acid shall be present. The determination may be made by weighing 0.1 gram, dissolving in a mixture of 70 cc. of water and 5 cc. of strong ammonia, adding 5 grams of 100-mesh zinc and 15 cc. of strong sulphuric acid, and finally titrating the reduced solution precisely as in a phosphorus determination (9).

The iron factor of the permanganate multiplied by 0.8598 will give the MoO_3 factor (11).

A yellow molybdate solution indicates the presence of silica, and a phosphorus determination made with such a solution is likely to come high, owing to ammonium silicomolybdate being dragged down with the phosphomolybdate. If about 30 milligrams of microcosmic salt dissolved in a little water be added per liter of yellow molybdate solution, the mixture agitated and then allowed to settle twenty-four hours, the solution will become colorless and fit for use.

13. **Method for Limestone.**—Treat 20 grams in a large covered beaker with sufficient strong hydrochloric acid to effect solution. Add

the acid cautiously, a little at a time, with agitation, to avoid frothing over the beaker. When enough acid has been added and effervescence has ceased, warm gently, if necessary, to dissolve any separated iron compounds. Solution being finally as complete as possible, dilute sufficiently with cold water and filter, washing filter and residue with cold water. To the filtrate add a few drops of ferric chloride solution (not necessary, of course, if the solution already contains sufficient iron) and then ammonia until the solution is alkaline to litmus paper. If the precipitate, containing the phosphorus as ferric phosphate, is not decidedly reddish-brown in color,* acidulate again with hydrochloric acid, add more ferric chloride solution and then ammonia once more to alkaline reaction. Now add acetic acid to decided acid reaction. Boil for a few minutes, filter, wash once with hot water and then dissolve in warm dilute hydrochloric acid on the filter, receiving the solution in the beaker in which the precipitation was made. Reserve this solution for the present.

14. The original insoluble residue may contain phosphorus. Ignite it in platinum until the carbon of the filter is all burned off, break up any lumps with a platinum rod and then ignite at a red heat for two or three minutes. Cool, moisten with water, add a little hydrochloric acid and warm to dissolve the soluble matter. Dilute and filter through the last filter used above, receiving the filtrate in the beaker containing the reserved solution. Dilute this solution and re-precipitate exactly as before with ammonia and acetic acid. Dissolve this precipitate on the filter in warm dilute hydrochloric acid, receiving the solution in a small beaker and washing the filter with hot water. Evaporate the solution in the beaker almost to dryness, to expel the excess of hydrochloric acid, and then add to it a filtered solution of 5 or 10 grams of citric acid (according to the size of the ferric precipitate) dissolved in 10–20 cc. of water. Next, add 5–10 cc. of magnesia mixture † and enough ammonia to make the liquid faintly alkaline. Stand

* Ferric phosphate is white and the red color indicates the necessary excess of iron precipitated as ferric hydroxide.

† *Magnesia mixture.*—Dissolve 110 grams of crystallized magnesium chloride ($MgCl_2 + 6H_2O$) in water and filter. Dissolve 280 grams of ammonium chloride in water, add a little bromine water, and a slight excess of ammonia, and filter. Add this solution to the solution of magnesium chloride, add enough ammonia to impart a decided odor, dilute to about 2 liters, shake vigorously from time to time, allow to stand for several days, and filter into a small bottle as required for use. Ten cc. of this solution will precipitate about 0.15 gram of P_2O_5. Blair, Chem. Anal. of Iron.

the beaker in cold water until perfectly cold and then add to the solution one-half its volume of strong ammonia and stir well. When the precipitate of NH_4MgPO_4 has begun to form, stop stirring and allow the beaker to stand in cold water for 10 or 15 minutes, then stir vigorously several times at intervals of a few minutes, and finally allow the mixture to stand over night. Filter on a small ashless filter and wash with a mixture of 1 part strong ammonia and 2 parts water, containing also 2.5 grams of ammonium nitrate in 100 cc.

15. Dry the filter and precipitate, and ignite them in a weighed platinum crucible, first at a very low temperature so as to carbonize the filter without decomposing the precipitate. Now break up the residue with a platinum rod and then heat at a gradually increasing temperature to the full power of a Bunsen burner, and continue the ignition until the residue is perfectly white. Cool and weigh. Now fill the crucible half full of hot water, add 5–20 drops of strong hydrochloric acid and heat until the precipitate has dissolved. Filter off on another small ashless filter any silica or ferric oxide that may remain, ignite and weigh. The difference between the two weights is the weight of the $Mg_2P_2O_7$, which, multiplied by 0.2787, will give the weight of the phosphorus.

16. **Method for Phosphorus in Tungsten Ores.**—Take 1 gram of the ore and fuse in a platinum dish with 5 grams of sodium carbonate and 1 gram of sodium or potassium nitrate. Disintegrate with hot water and filter, washing with hot water. If much silica is present, acidify the filtrate with hydrochloric acid, evaporate to dryness, take up in hydrochloric acid and water, in the usual way for silica, and filter, washing with dilute hydrochloric acid. If there is but little silica, its removal may be omitted and the filtrate from the fusion simply made acid with hydrochloric acid. To the acid solution (which may contain a precipitate of WO_3) add sufficient ferric chloride solution to color the liquid a distinct yellow, avoiding a great excess. Now make strongly alkaline with ammonia, boil and filter, washing well with hot water. Dissolve the precipitate, after rinsing most of it back into the beaker, with hydrochloric acid, pouring the solution through the same filter, and wash out every trace of iron with warm dilute hydrochloric acid. Dilute the filtrate somewhat with hot water and re-precipitate the iron with ammonia as before. Filter, washing the precipitate at least ten times with hot water. Dissolve the precipitate on the filter with a hot mixture of 10 cc. of strong nitric

acid and 20 cc. of water, washing out every trace of iron with hot, dilute nitric acid. Receive the filtrate in an 8-oz. flask. Boil to about 40 cc., or less, if the bulk is larger. Precipitate the phosphorus with molybdate solution in the usual way (1). Filter through a weighed Gooch crucible. Multiply the weight of the yellow precipitate by 0.0163 to obtain the phosphorus.

CHAPTER XXIII

POTASSIUM AND SODIUM

1. Method of J. Lawrence Smith for Silicates.—*Principle.*—The substance is heated with a mixture of 1 part ammonium chloride and 8 parts calcium carbonate. By this means the alkalies are obtained in the form of chlorides, while the remaining metals are for the most part left behind as oxides, and the silica is changed to calcium silicate, as represented by the following equation:

$$2KAlSi_3O_8 + 6CaCO_3 + 2NH_4Cl \rightarrow 6CaSiO_3 + 6CO_2 + Al_2O_3 + 2KCl + 2NH_3 + H_2O.$$

The alkali chlorides together with the calcium chloride can be removed from the sintered mass by leaching with water, while the other constituents remain undissolved.

Preparation.—The ammonium chloride necessary for the determination is prepared by subliming the commercial salt; the calcium carbonate, by dissolving the purest calcite obtainable in hydrochloric acid and precipitating with ammonia and ammonium carbonate. This last operation is performed in a large porcelain dish. After the precipitate has settled, the clear solution is poured off and the precipitate is washed by decantation until free from chlorides. The product thus obtained contains traces of alkalies, but the amount present is determined once for all by a blank test, and a corresponding deduction made from the results of the analysis; it is usually sodium chloride and amounts to 0.0012–0.0016 gram for 8 grams calcium carbonate. The decomposition was performed by Smith in a finger-shaped crucible about 8 cm. long, with a diameter of about 2 cm. at the top and 1½ cm. at the bottom. Such a crucible is suitable for the decomposition of about 0.5 gram of the mineral. A larger quantity can be analyzed in an ordinary platinum crucible.

Filling the Crucible.—Mix 0.5 gram of the finely ground mineral with 0.5 gram of sublimed ammonium chloride, by trituration in an

agate mortar; then add 3 grams of calcium carbonate and mix intimately with the rest. Transfer to a platinum crucible with the help of glazed paper. Rinse the mortar with 1 gram of calcium carbonate and add the rinsings.

The Ignition.—If a Smith crucible is used it is placed in a slightly inclined position for heating. This is best done by inserting the covered crucible through a hole in the side of a fire-clay cylinder, such as a large crucible with the bottom cut away. The top of the platinum crucible projects from the side and is thus protected from the flame. Heat gradually over a small flame until no more ammonia is evolved.* This should take about fifteen minutes. Now increase the heat until finally the lower three-fourths (and no more) of the crucible is brought to a dull red. Maintain this temperature for fifty or sixty minutes. After cooling, the sintered cake can usually be removed by gently tapping the inverted crucible. Should this not be the case, add a little water and warm gently for a few minutes to soften the cake; then wash it into a large porcelain, or, better, platinum dish. Add 50–75 cc. of hot water and heat the covered dish for half an hour, replacing the water lost by evaporation. Reduce the large particles to fine powder by rubbing with a pestle in the dish. Finally, decant the clear solution through a filter, wash the residue four times with hot water by decantation; then transfer to the filter and wash with hot water until a few cubic centimeters of the washings give only a slight turbidity with silver nitrate. To make sure that the decomposition of the mineral has been complete, treat the residue with a little hydrochloric acid. It should dissolve completely.

Instead of the Smith design, an ordinary large platinum crucible may be employed for the ignition. Place the crucible in a hole cut in a sheet of asbestos. The hole should be of such a size that not more than two-thirds of the crucible will be exposed below. Conduct the heating and other operations in accordance with the description given above.

In the case of either crucible, actual fusion of the mass should not occur. The $CaCl_2$ formed by the reaction between the NH_4Cl and the $CaCO_3$ attains a state of fusion and is absorbed by the large excess of $CaCO_3$ present. Actual fusion of the silicate would render subse-

* During this part of the operation the heat should be kept so low that ammonium chloride does not escape. The latter is dissociated into ammonia and hydrochloric acid by the heat, and the acid unites with the calcium carbonate to form calcium chloride.—(Treadwell's Analytical Chemistry [Hall], Vol. II.)

quent disintegration of the mass impossible. When fusion of the mass occurs, in spite of the low temperature maintained, it may be due to the fusible nature of certain silicates, notably those containing much ferrous iron. In such a case it is better to begin anew and increase the proportion of $CaCO_3$ to 8–10 parts.

Precipitation of the Calcium.—Treat the aqueous solution with ammonia and ammonium carbonate, heat and filter. The precipitate retains small amounts of alkali. Dissolve it in hydrochloric acid and repeat the precipitation with ammonia and ammonium carbonate. Combine the filtrates and evaporate to dryness in a porcelain or platinum dish. While the major portion is evaporating, transfer it in portions to a smaller dish, where the evaporation is continued, finally rinsing all into the small dish. When the final dry residue is obtained in the small dish, cover the dish and heat it for a while in a drying-oven at 110° C. This lessens the danger of subsequent loss by decrepitation. Now expel the ammonium salts by careful ignition over a moving flame. Allow to cool, dissolve the residue in a little water, heat and add a little ammonia and ammonium oxalate to remove the last traces of calcium. After it has stood for twelve hours, filter off the calcium oxalate, receiving the filtrate in a weighed platinum dish. Evaporate it to dryness, cover it, and heat it, still covered, in an oven at 110° C.; then ignite gently to expel ammonium salts. Cool, moisten with hydrochloric acid to convert any carbonate into chloride, and then repeat the evaporation and ignition with the same precautions as before. Determine the weight of the contents of the dish, which represents the amount of alkali chloride present. To determine potassium, dissolve the residue in a little water and precipitate as potassium platinic chloride, as described in 7, 8. The sodium is determined by difference.

2. **Variation from above Procedure.***—In the official method of the Assoc. Official Agr. Chemists, the procedure, after the filtrate from the disintegrated sintered mass has been obtained, is as follows:

Precipitate the calcium with ammonia and ammonium carbonate, allow to settle and then concentrate the supernatant solution, decanting in portions if necessary, in a small porcelain or platinum dish, finally rinsing in the precipitate. When the whole is thus reduced in the small dish to about 30 cc., add a little more ammonia and ammonium carbonate. Evaporate to dryness on a water-bath, expel the

* From Griffin's "Methods of Technical Analysis."

ammonium chloride by gentle ignition, and dissolve the residual alkali chlorides in 3–5 cc. of water.

A little black or dark brown flocculent matter usually remains undissolved, and the solution may still contain traces of calcium. Add 2 or 3 drops of ammonia and ammonium carbonate, warm gently and filter through a very small filter into an unweighed but weighable platinum dish. Evaporate to dryness on a water-bath, heat at dull red to incipient fusion of the alkali chlorides, and after cooling, weigh. Dissolve the mixed chlorides in a little water and filter through a small filter into a porcelain dish. Ignite the filter in the platinum dish previously used, and weigh. Subtract this weight from the first weight to obtain the weight of the NaCl+KCl.

Determine the K_2O in the filtrate in the porcelain dish by precipitating with platinum chloride (7, 8), adding sufficient platinum chloride to combine with the total weight of alkali chlorides calculated as NaCl, i.e., an amount of metallic platinum 1.67 times the weight of alkali chlorides found.

3. **Hydrofluoric Acid Method.**—Treat 1 gram of the finely powdered silicate in a platinum dish with pure strong hydrochloric and hydrofluoric acids until decomposition is complete. It is best to add the hydrochloric acid first, to prevent spattering, and then to add about an equal amount of hydrofluoric acid and warm gently. Finally, evaporate to dryness on the water-bath, then add a little dilute hydrochloric acid and evaporate again to dryness.

4. Dissolve the residue in hot water, add 5 cc. of a saturated solution of barium hydroxide, and heat to boiling. Allow to settle a short time and then test the clear liquid with a little more barium hydroxide solution, to be certain that enough has been added. When the precipitation is complete, filter and wash well with hot water. Heat the filtrate to boiling and add a little ammonia and ammonium carbonate to complete the precipitation of calcium, barium, etc., and, after allowing to stand a short time on the water-bath, filter and wash the precipitate thoroughly with hot water.

5. Evaporate the filtrate to dryness in platinum or porcelain and then expel the ammonium salts by a heat just below redness. Take up the cool residue in a little hot water, add a few drops of ammonia, a drop or two of strong ammonium carbonate solution and a few drops of ammonium oxalate solution. After allowing to stand a short time

on the water-bath, set aside for a few hours and then filter, washing with hot water.

6. Evaporate the filtrate to dryness on the water-bath and heat the residue to dull redness until all ammonium salts are expelled and it has become nearly or quite white. Cool, dissolve in a very small amount of water and filter into a weighed platinum dish. Add a few drops of hydrochloric acid and evaporate to dryness on the water-bath. Heat the residue to dull redness, cool in a desiccator and weigh as mixed potassium and sodium chlorides. Repeat the heating until a constant weight is obtained. Dissolve the chlorides in a small amount of water. If a residue remains undissolved, the separation must be repeated until the chlorides finally obtained are entirely soluble.

Proceed with the solution of the chlorides as described in **7** or **10**.

SEPARATION OF POTASSIUM AND SODIUM

7. **Direct Method.**—It is assumed that the two metals are in aqueous solution as chlorides in a platinum or porcelain evaporating dish, the weight of the mixed chlorides being known. Add a slight excess of hydrochlorplatinic acid (H_2PtCl_6) and evaporate to dryness at a low temperature on a water-bath in which the water is not boiling. The drying is to dehydrate the sodium platinic chloride and render it more soluble in alcohol. It is a good plan to have the platinum solution contain 10 per cent of platinum, i.e., 1 gram in every 10 cc., and, in order to use the right quantity and avoid unnecessary excess, make the following calculation:

Assume that the mixed chlorides consist entirely of NaCl. Call their weight a. Then from the formula $Na_2PtCl_6+6H_2O$ we find that 46 parts of Na require 195.2 parts of Pt. 46 parts of Na correspond to 116.92 parts of NaCl; therefore we have the proportion

$$116.92 : 195.2 = a : \text{Pt required}$$

Solving this and multiplying the result by 10, we arrive at the number of cubic centimeters of platinum solution required. Always add 0.3–0.4 cc. in excess.

It is necessary to convert all the sodium, as well as the potassium, to the platinum compound, as otherwise the undecomposed sodium chloride, being insoluble in absolute alcohol, would contaminate the potassium platinic chloride; the calculation is therefore made as above.

8. After the evaporation, add to the cool residue a few cubic centi-

meters of absolute alcohol (methyl alcohol is the best) and thoroughly disintegrate the solid mass with a stirring-rod or platinum spatula. Decant the clear liquid through a filter moistened with alcohol, and then repeat the stirring with fresh portions of alcohol, until a perfectly colorless filtrate is obtained and the remaining salt in the dish is pure golden-yellow with no intermixed orange-colored particles of Na_2PtCl_6. The latter compound is soluble in the alcohol while the corresponding potassium salt is not. Transfer the washed residue to the filter, allow to drain completely and then dry in an air-bath at 80°–90° C. When dry, carefully transfer as much of the precipitate as possible to a watch-glass. Replace the filter in the funnel and dissolve the adhering precipitate (and also any in the original dish) by washing with a little hot water, receiving the filtrate in a weighed platinum dish or crucible. Evaporate the solution to dryness at a low temperature on the water-bath and then add the precipitate on the watch-glass. Dry the whole at 160° C. and weigh as K_2PtCl_6. Multiply this weight by 0.30561 to obtain that of the KCl. Although this factor is correct according to the less recent values of the atomic weights, the factor 0.30673 is the correct one according to the latest values. This figure, however, does not actually give results so near to the truth as the older factor. This is due to the fact that our assumption as to the formula K_2PtCl_6 is not quite correct. Changes are produced by the evaporation which are compensated for by the use of the old factor.

Having determined the weight of the KCl in the mixed chlorides, the difference from the total weight is the NaCl.

Multiply the weight of the KCl by 0.632 to obtain the weight of the K_2O.

Multiply the weight of the NaCl by 0.5303 to obtain the weight of the Na_2O.

9. Indirect Method.—This method is accurate only when both bases are present in considerable amount.

The metals must first be obtained as chlorides by one of the preceding methods, and the combined weight noted. Now determine the percentage of chlorine in the mixture (see XI, 1) and then apply the following rule:

Subtract 47.54 from the percentage of chlorine in the mixture. Divide the remainder by 0.1312. The result is the per cent of sodium chloride in the mixture.

The rule is determined as follows: Pure NaCl contains 60.66 per cent of Cl. Pure KCl contains 47.54 per cent of Cl. The difference between the two percentages is 13.12. This 13.12 per cent excess represents, then, 100 per cent of NaCl; therefore every 0.1312 per cent above 47.54 represents 1 per cent of NaCl; hence the above rule.

10. Separation of Potassium and Sodium by the Perchlorate Method.—It is assumed that the two metals exist as chlorides in a platinum or porcelain dish, the weight of the mixed chlorides being known. Add just enough water to dissolve the salts, then 5 cc., or more, of 20 per cent perchloric acid and evaporate to dryness on a hot-plate and until all fumes of perchloric acid have disappeared. If the heavy fumes fail to appear, cool, again take up in a little water, add 5 cc. more of perchloric acid and repeat the evaporation. Two evaporations, each showing the heavy fumes, are necessary, the fumes being entirely expelled each time. Finally, allow to become completely cool and then continue as described in **13, 14**. Multiply the K_2O found by 1.582 to obtain the KCl. Subtract this from the weight of the mixed chlorides to obtain the weight of the NaCl. Multiply this by 0.5303 to obtain the Na_2O.[1]

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[1] The potassium in K_2O is sufficient to form $2KCl$, or, $K_2O = 2KCl$. Molecular weight of $K_2O = 94.2$. Molecular weight of $KCl = 74.56$. $2KCl = 149.12$. Then, $94.2\ K_2O = 149.2$ KCl, or, $1\ K_2O = 1.582$ KCl. Similarly, $2NaCl = Na_2O$, or, 116.92 NaCl $= 62\ Na_2O$. This gives 1 NaCl $= 0.5303\ Na_2O$.

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11. Short Perchlorate Method for Soluble Potash.—In the case of water, weigh 50 grams, more or less, according to supposed richness, and evaporate to dryness in a small weighed porcelain or platinum dish. Heat the residue for some time at about 150° C., cool, and weigh, This gives the per cent of salts in the water. If the weight is small, 0.5 gram or less, all may be used and dissolved right in the dish. If considerably more than 0.5 gram, grind to powder in the dish with an agate pestle, and weigh out 0.5 gram for the analysis. Continue as described below.

12. In the case of salts, such as mixtures of sulphates, chlorides and carbonates, have the material finely ground and well mixed. Using a weighing-bottle, weigh something more than 0.5 gram into it. Dry this at 150° C. This gives the moisture and the weight of dry

substance. Wash the material into a small beaker, add a drop of methyl orange, cover the beaker and make just acid with hydrochloric acid. If filtration appears advisable, boil a moment if CO_2 has been shown, and then filter through a small filter into a beaker. Wash six times with hot water. Dilute the filtrate, or boil it down, as may be necessary, to 50 cc., and add an excess of 3/20 cc. of strong hydrochloric acid. Heat to boiling and add 10 per cent barium chloride solution in slight excess. Take time to do this carefully, as a large excess of barium chloride is troublesome in subsequently converting to perchlorate. The hot liquid may be filtered immediately into a shallow evaporating-dish, washing with hot water. Any small amount of barium sulphate that has failed to separate will do no harm. Add 5 cc. of 20 per cent perchloric acid and evaporate to dryness on a hot-plate and until fumes of perchloric acid have ceased. Cool sufficiently, wash down the sides of the dish with just enough hot water to dissolve the salts, add 1 or 2 cc. more of perchloric acid and again evaporate as before. If no fumes of perchloric acid appeared on the first evaporation, add 5 cc. for the second evaporation and again repeat with 1 or 2 cc.

13. Allow to become completely cold, then add 25 cc. of a saturated solution of potassium perchlorate in 95 per cent grain alcohol (or denatured alcohol). Cover the dish and allow a little time for the soluble perchlorates to dissolve. The final salts consist of the perchlorates of the bases present, of which only potassium perchlorate is insoluble in the alcohol, mixed perhaps with barium sulphate and small amounts of organic and other insoluble matter.

14. Prepare a Gooch crucible with a thick asbestos mat and have it dry. Thoroughly loosen up the salts in the dish with a rubber-tipped glass rod, rubbing the particles so as to leave only a powdery residue, free from lumps. Rub a little grease on the lower side of the lip of the dish, as the alcohol has a tendency to run down the outside, and filter through the Gooch (not yet weighed). Using the alcoholic perchlorate solution in a small wash-bottle, transfer all the residue from the dish to the filter, allow all the liquid to run through, and then wash six times with the alcoholic perchlorate solution, allowing to drain completely each time. Finally, drain thoroughly and then dry in an oven at 130°–150° C., cool and weigh. Now wash the residue in the Gooch six times with hot water, which will dissolve the potassium perchlorate, then twice with alcohol, and once with a very little

of the alcoholic perchlorate solution. Drain completely, dry, cool and weigh as before. The loss in weight represents the potassium perchlorate. Multiply this by 0.3399 to obtain by K_2O.[1]

The alcoholic perchlorate solution is made by simply shaking up an excess of potassium perchlorate with the alcohol, allowing to stand some time, best overnight, and always shaking the mixture and filtering or decanting a portion before use, so as to have the solution saturated at the laboratory temperature when used.

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[1] $2KClO_4 = K_2O$. Molecular weight of $KClO_4 = 138.56$. $2KClO_4 = 277.12$ Molecular weight of $K_2O = 94.2$. Then, 277.12 $KClO_4 = 94.2$ K_2O, or, 1 $KClO_4 = 0.3399$ K_2O.

CHAPTER XXIV

SILICA

In the valuation of ores, it is often customary to designate as "silica" the insoluble residue remaining after certain conventional treatments with acids. Precautions are taken to remove lead compounds and sometimes other efforts at purification are made, so that the final insoluble residue, or so-called "silica," shall consist mainly either of fairly pure silica or a mixture of silica and undecomposed silicates.

1. Insoluble Residue or "Silica" in Ores, etc.*—Weigh 0.5 gram of the ore into a 250 cc. Pyrex beaker. The choice of acids for the decomposition will depend upon the apparent nature of the ore. Oxidized ores, especially when they contain much iron or manganese, should first be treated with hydrochloric acid alone, say 10 or 15 cc., and the mixture warmed very gently until decomposition and solution are as complete as possible. Actual boiling should be avoided, as the acid is thereby weakened and rendered less effective. If sulphides finally remain undissolved, add a few cubic centimeters of strong nitric acid and heat the mixture again.

If the ore is largely a sulphide it may frequently be attacked at once with 10 cc. of strong nitric acid, and the mixture warmed gently until the first violent action has somewhat subsided. Then add 5 cc. of strong hydrochloric acid and continue the warming to complete the decomposition if necessary.

In the case of very heavy sulphides, where the separated sulphur, after treatment with nitric acid, appears to be still impure, it may be advisable to add small portions of potassium chlorate from time to time, together with more nitric acid if necessary, and continue the heating until the sulphur is either entirely oxidized or sufficiently purified. Then add 5 cc. of strong hydrochloric acid, very cautiously,

* See **21.**

to avoid too violent action with the undecomposed chlorate, and again heat gently.

2. When a sufficiently complete decomposition has been obtained by any of the above methods, or modifications of them suggested by the nature of the ore in hand, the solution is to be evaporated to complete dryness. This may be done by gentle heating on a hot plate or water-bath.

When the mixture has become dry, continue the heating for five or ten minutes, or more, at a temperature of about 150° C., in order to dehydrate any gelatinous silicic acid present. Finally, after cooling somewhat, add 10 cc. of strong hydrochloric acid and warm until solution is as complete as possible. Now add 40 cc. of water and about 5 grams of ammonium chloride. The latter is to hold lead salts in solution and may of course be omitted when no lead is present. Heat to boiling and see that everything soluble is properly dissolved. Filter through a 9-cm. filter and wash well with hot water. It is best either to have the water slightly acidulated with hydrochloric acid, or to wash at least once or twice with acidulated water, to remove from the filter any insoluble iron compound due to the hydrolysis of ferric chloride. Any residue adhering in the beaker should be dislodged with a rubber-tipped glass rod and rinsed into the filter. Ignite and weigh.

3. It is usually sufficient to place the filter and contents, without drying, in a small clay " annealing-cup " or a porcelain crucible and ignite in a muffle or over a Bunsen burner. When cold, shake and brush the ignited residue upon the scale-pan and weigh. The weight of the filter-ash may ordinarily be neglected. As 0.5 gram of ore was taken, the weight in centigrams multiplied by 2 will give the percentage of " silica."

4. When the methods above described fail to effect a fairly complete decomposition of the ore, sulphuric acid may be tried in addition. Proceed in the usual way with hydrochloric and nitric acids until decomposition is about as complete as possible, and then add 5 cc. of strong sulphuric acid and heat (preferably over a free flame) until the white fumes are coming off copiously. It is best to continue the heating until most of the sulphuric acid is expelled. Cool, dilute with about 40 cc. of water, add 5 cc. of strong hydrochloric acid and 5 grams of ammonium chloride, and boil to effect solution of everything soluble. Finally, filter, wash, ignite, and weigh as described above.

If an ore contains silicates that are gradually but appreciably decomposed by acids, it is evident that the amount of insoluble residue obtained will depend largely upon the length of time employed in the treatment. This trouble, which is inherent in the method, does not often occur to a very appreciable extent, and the results obtained by different operators ordinarily agree fairly well.

5. Barium in the Insoluble Residue.—If an ore contains barium sulphate the latter will, of course, be found with the insoluble residue. Any soluble barium mineral in the presence of sulphates or sulphides will also be either wholly or partly changed to sulphate, which will remain behind. When the insoluble residue is thus contaminated with barium sulphate, it is customary to determine the same and deduct it. This may be done as follows:

Fuse the mixed residue, after weighing, with about 3 grams of sodium carbonate, or mixed sodium and potassium carbonates, in a platinum dish or crucible. Prolonged fusion is not necessary, as the object is simply to convert the barium sulphate to carbonate. After cooling, heat the fused mass with water until disintegration is complete, and then filter through a 9-cm. filter and wash thoroughly to remove sulphates. The barium is left on the filter as carbonate, probably more or less impure. A little barium carbonate may also remain adhering to the platinum dish. Dissolve the latter in 5 cc. of strong hydrochloric acid diluted with about 10 cc. of water, and, if the amount of carbonate on the filter is small, dissolve it by pouring the acid mixture (preferably warmed) over it from the dish, receiving the filtrate in a large beaker. If the quantity of carbonate is large, rinse it from the filter to a small beaker and dissolve it by adding the acid in the dish, keeping the beaker covered with a watch-glass to prevent loss by spattering. Warm the solution and pour it through the filter to dissolve any carbonate remaining thereon. Wash the filter well with hot water. Dilute the filtrate to about 300 cc. with hot water, heat to boiling and precipitate the barium as sulphate, in the usual way (consult BARIUM, 1), with dilute sulphuric acid. After it has stood until cold, filter off the barium sulphate, wash with hot water, ignite, and weigh. The weight found, deducted from that of the original mixture, will leave the weight of the insoluble residue required.

6. Treatment of Ores and Slags that Gelatinize with Acids.—Some ores and furnace products are more or less completely decom-

posed by acids with the formation of gelatinous silica. Slag that has been suddenly chilled by dipping an iron bar into the molten mass and then plunging it with the adhering slag into cold water, may usually be entirely decomposed by acids. Roasted ores generally give gelatinous silica. If such substances are treated in the usual way, the gelatinous silica is liable to form a cake which adheres to the bottom of the beaker and greatly hinders decomposition by surrounding particles of the ore with a more or less impervious coating. Material of this class may be treated as follows:

Moisten the 0.5 gram of substance in the beaker (a 4-inch porcelain casserole or dish is better) with 2 or 3 cc. of water, and then add gradually about 10 cc. of strong hydrochloric acid, stirring or shaking the mixture at the same time to prevent coagulation. Cover the dish with a watch-glass and heat very gently with frequent stirring, until decomposition is as complete as possible, adding a little nitric acid if undecomposed sulphides still remain. Finally, remove and rinse off the cover, evaporate to dryness and finish in the usual way (2).

In the case of chilled slag, the silica thus obtained is fairly pure. When there is much gelatinous silica, especial pains should be taken in the heating after evaporation so as to dehydrate it as thoroughly as possible. In technical work it usually suffices to heat the dry residue for half an hour or an hour, at a temperature of about 150° C. (cf. 10).

7. **"True Silica" or "Silica by Fusion."*** (Also see 20).—These terms, in technical work, refer simply to the silica obtained by technical methods when the decomposition of the substance includes a fusion with alkali carbonate. The result is ordinarily much more accurate as regards actual silica than that obtained by the usual acid treatment, but it is not customary to follow all the requirements of exact analysis. In the case of ores containing considerable matter soluble in acids, or constituents undesirable in the fusion, such as sulphides and compounds of reducible metals, it is usually best to give a preliminary treatment with acids and confine the fusion to the residue finally obtained, which may consist of mixed silica and undecomposed matter. Such ore is decomposed and treated, according to its nature, precisely as described for INSOLUBLE RESIDUE (2) and the residue, containing the total silica of the substance, ignited in a

* Insoluble silicates, such as clays, etc., are usually decomposed by this method. In accurate analyses the procedure may be according to 19.

platinum dish or crucible to burn off the filter-paper. It need not be weighed.

8. Mix the ignited "insoluble residue," or 0.5 gram of the finely pulverized ore or silicate, if no preliminary treatment was given, in a platinum crucible or small platinum dish with about 5 grams of sodium carbonate, or a mixture of 3 parts of sodium carbonate and 2 parts of potassium carbonate, which fuses more easily. If the ore, not subjected to previous acid treatment, contains, or is likely to contain, a small amount of sulphides, mix in a small pinch of potassium nitrate to insure their oxidation. Heat the mixture over a blast-lamp, very slowly at first, so as to expel moisture without mechanical loss of substance. Raise the heat very gradually, so that much of the carbon dioxide may be driven off without causing any spattering, before the mass has actually fused to a liquid. Finally heat strongly to complete fusion of the mixture and continue the heating until bubbling has practically ceased and quiet fusion is attained. In some cases this takes from half an hour to an hour. If a crucible is used it is best to keep it covered to prevent loss from spattering; with a dish there is less danger. Cool the crucible or dish and digest the fused mass with hot water. As a crucible is too small to contain sufficient water, it is best to place it in a 6-inch porcelain dish, first detaching the cake, if possible, as follows: The crucible having been chilled quickly by dipping the bottom in cold water, a minute crack will usually develop between the sides of the cake and the crucible. Allow a drop or two of water to fall into this crack and then cautiously heat the crucible over a lamp. Under these conditions the cake will usually detach itself with a slight "pop." Place the crucible and cake in the evaporating-dish and warm with water until disintegration is as complete as possible. Now remove and rinse off the crucible and cover. If the crucible is not perfectly clean inside, dissolve the adhering residue with a little hydrochloric acid and add the solution to the main portion in the dish, after the latter has been acidified. If a platinum dish has been used instead of a crucible, warming in the dish with one or two portions of water will usually suffice for disintegration and transfer to the porcelain dish. The last traces of residue may be removed by the acid used for acidifying.

9. Cover the evaporating dish and cautiously add hydrochloric acid in excess. It is not a good plan to add the acid before removing the platinum, since when manganese is present chlorine may be

evolved and may attack the platinum if the latter is exposed for any length of time. Nitric acid can be used and the danger avoided, but it is not so desirable a solvent.

Warm the mixture in the dish, and when the effervescence has sufficiently subsided remove and rinse off the cover and then support it on a glass triangle placed on the dish so as to allow a free circulation of air over the liquid. If the fusion has been successful and the decomposition is complete, practically everything should dissolve in the acid liquid and no hard, gritty, or dark particles should remain in the bottom of the dish.

10. The solution must now be evaporated to dryness. This may be done on a water-bath or as otherwise convenient,* except that care must be taken not to overheat at the end. When the mass is dry, remove the triangle and place it on top of the watch-glass and the latter directly on the dish. This is to prevent loss by any subsequent decrepitation. Heat now over a radiator or in an air-bath, at a temperature of about 150° C., for thirty minutes or more. The residue should finally appear perfectly dry and powdery under a glass rod. It is impossible to render the silica perfectly insoluble, so as to remove it pure at one operation, by any modification of the heating, but for ordinary technical results the above directions will suffice. Too high a temperature will cause a recombination of some of the silica with the bases present, and then, on the addition of acid, some of this silica will again be set free in a soluble form.

11. To the dried mass add about 20 cc. of strong hydrochloric acid and allow to stand, covered, at the ordinary temperature or slightly warmed, for about ten minutes; then add about 100 cc. of hot water and heat to boiling, first removing and rinsing off the cover and triangle. After boiling a moment, allow the silica to settle and decant the clear liquid through a filter. It is best to wash the silica once or twice by decantation with hot water and then transfer it to the filter and finish the washing. If the upper edge of the filter appears brown, from the separation of a basic ferric compound, due to hydrolysis of ferric chloride, wash with warm dilute hydrochloric acid until clean.

Place the moist filter and contents in a weighed platinum crucible and ignite until perfectly white. Cool in a desiccator and weigh.

* With a water-bath the operation is sometimes very tedious. I usually support the dish on a scorifier placed in an iron sand-bath dish or radiator and have a low flame under the latter.

12. Testing the Weighed Silica.—When it is desired to test the purity of the silica obtained, it may be done as follows: Cover the silica in the platinum crucible or dish with 2 or 3 cc. of water to prevent violent action, and then add 2 or 3 drops of strong sulphuric acid and 3 to 5 cc. of pure hydrofluoric acid. Evaporate the mixture as far as possible on a water-bath, and then heat cautiously over a small free flame to complete dryness. If there is a residue add a little more hydrofluoric acid and again evaporate. Repeat this procedure until no residue remains, or until there is no further diminution of the residue obtained. In the latter case, add a drop or two of strong sulphuric acid, heat to dryness and ignite strongly over the blast-lamp, cool, and weigh. Unless the amount of residue thus found is large, it will usually be sufficient to deduct its weight from that of the impure silica to obtain the true silica.

Barium sulphate in an ore would naturally contaminate the silica. Its amount could be determined and deducted as just described, or the weighed impure silica could be fused with alkali carbonate and the barium determined as sulphate, as described in 5.*

13. Determination of Silica in Ores Containing Fluorine.—Substances containing fluorine will sustain a loss of silicon by volatilization as fluoride, if the solution from the carbonate fusion is subjected to the usual evaporation with acid. The following methods are applicable in such cases.

14. Seeman's Method.†—Fuse with alkali carbonate as directed in 8. Extract the melt with hot water and filter from the insoluble residue. Any barium present will remain with the residue as carbonate. Make the filtrate faintly acid with hydrochloric acid and then add an excess of a solution of mercury ammonium carbonate. Evaporate the mixture to dryness, add water to the residue and again evaporate to dryness. Take up the residue in hot water. It is easily filtered and washed and may be directly ignited and weighed to obtain the anhydrous silica.

The mercury-ammonium carbonate may be prepared by adding to a quantity of mercuric oxide a sufficient excess of a cold saturated solution of ammonium carbonate to form a clear solution.

* A more common method at western smelting-works is to filter the aqueous solution of the melt of the original fusion before acidifying. The barium is thus practically all removed as carbonate at this point.

† F. Seeman, Ziet. f. anal. Chem., LXIV, 343–387.

15. Method of Berzelius.—Thoroughly extract the melt from the alkali carbonate fusion (8) with hot water and filter from the insoluble residue. (Any barium will remain behind as carbonate.) To the filtrate add about 4 grams of solid ammonium carbonate, heat for some time at about 40° C. and then allow to stand overnight. Filter off the precipitate and wash with water containing ammonium carbonate. Reserve the silica thus obtained.

Some silica still remains in the filtrate. To recover this, add to the solution 1 or 2 cc. of ammoniacal zinc oxide solution (made by dissolving moist zinc oxide in ammonia water), boil until the ammonia is all expelled and then filter off the precipitate of zinc silicate and oxide and wash with water. Spread out the filter on a watch-glass, and, with a jet from the wash-bottle, rinse as much of the precipitate as possible into an evaporating-dish. Pour a little dilute hydrochloric acid over the filter and any remaining residue, letting it run into the dish, then burn the filter and add the ash. Add a little more hydrochloric acid to the contents of the dish, if necessary to decompose and precipitate, and then evaporate on the water-bath and separate the silica as usual (10). Filter off this silica and reserve it.

The insoluble part of the melt may contain silica. Dissolve it in hydrochloric acid and separate the silica by evaporation as usual. (Any barium will pass into the filtrate as chloride.)

Finally ignite and weigh all three silica precipitates together.

16. Decomposition of Silicates by the Lead Oxide Method of Jannasch.—This method is applicable in the case of pure silicates and admits of determination of the alkalies in the same portion. Pure lead oxide is required, but as the commercial article is not safe, it is best to use the carbonate, which is converted into the oxide by ignition. It may be prepared as follows: To a boiling solution of lead acetate add the theoretical amount of ammonium carbonate. Wash the precipitated lead carbonate several times by decantation with hot water, then transfer it to a hardened filter (to avoid contamination with loosened fibers), wash completely, and allow to drain thoroughly, or better, use suction. Carefully remove from the filter and dry completely in a porcelain dish on the water-bath.

17. Mix 1 gram of the very finely powdered substance with 10–12 grams of lead carbonate. Place the carbonate in the crucible first, then add the weighed substance and mix very thoroughly with a platinum spatula. Cover the crucible and heat gently, below the

fusing-point of the mixture, for fifteen or twenty minutes, to expel most of the carbon dioxide. Now heat more strongly, being careful to have a non-luminous oxidizing flame, until the fusion is complete and keep it at this temperature for ten or fifteen minutes. Only the lowest third of the crucible should be heated to redness. Cool the crucible quickly by dipping the bottom in hot water, then place it, together with the cover, in a platinum dish and cover with hot water. After adding sufficient strong nitric acid to insure solution of the lead, heat on a water-bath until disintegration is complete. Remove the crucible and cover when the adhering portions of the melt have dissolved or separated therefrom. To assist in the disintegration, stir the mixture frequently and break up hard lumps as much as possible. Only slightly colored flocks of silicic acid should finally remain floating in the liquid. Now evaporate to complete dryness. Moisten the dry mass with strong nitric acid and again evaporate to dryness. Add 20 cc. of strong nitric acid to the dry residue, allow to stand fifteen minutes and then add 100 cc. of water. Heat the mixture for twenty minutes on the water-bath and then filter. Wash the silicic acid first with hot water acidulated with nitric acid, and then with pure hot water. Ignite and weigh in the usual manner.

18. Common Errors in the Determination of Silica.—Under this heading Dr. Hillebrand has published an exhaustive paper in Vol. XXIV of the Journal of The American Society. While the technical chemist, working by conventional methods, might regard his findings as of minor importance, they should nevertheless always be borne in mind. They are as follows:

1. Silica cannot be rendered wholly insoluble by any number of evaporations with hydrochloric acid when followed by a single filtration, no matter what temperature may be employed. Two or more evaporations alternating with filtrations are necessary to secure satisfactory results.*

2. The generally accepted view, that silica passing into the filtrate is wholly thrown down by ammonia or sodium acetate in presence of much alumina or iron, is incorrect.

3. Silica is appreciably soluble in melted potassium pyrosulphate, and consequently, when silicious oxides of iron and aluminum obtained

* Hillebrand (private communication) says: "Where I have fused a gram of rock (silicate) with 4–6 grams of sodium carbonate, I always recover about 3 milligrams of silica from the iron and alumina, even after two evaporations and filtrations."

in analysis are thus fused, their silica contents are only in small part left undissolved when the fused mass is taken up with water or acid. These last two sources of error may be avoided by separating all silica at the start as above.

4. The need of long blast ignition of the silica in order to get the correct weight is proved, continual loss of weight being invariably observed for thirty minutes or more.

19. Accurate Method for Silica.—Treadwell,* for an accurate silica determination, directs as follows: Evaporate the dilute hydrochloric acid solution of the residue after the fusion, or the original material, if entirely decomposed by acid, in a porcelain dish, to dryness, on the water-bath.† Stir frequently until the residue is obtained as a dry powder. Moisten this with strong hydrochloric acid, cover the dish and allow to stand at least twenty minutes at the ordinary temperature, to insure the changing to chlorides of any basic salts or oxides formed during the evaporation. Then add 100 cc. of water, heat to boiling, allow the silicic acid to settle and decant the clear liquid through a filter supported upon a platinum cone in a funnel. Wash the residue three or four times by decantation with hot water, then transfer to the filter and wash with hot water until free from chloride. If the silicic acid is not perfectly white, but brownish from basic ferric salt, drop strong hydrochloric acid around the upper edge of the filter and immediately wash it down with a stream of hot water. Repeat this until the filtrate comes through perfectly colorless. Finally, dry the precipitate by suction, place it in a platinum crucible and set it aside for the time being. The separation of the silica is now by no means quantitative; as much as 5 per cent of the total amount may remain in the filtrate. To remove this, evaporate the solution once more on the water-bath to dryness, keep at this temperture for one or two hours (or more), moisten with a few cubic centimeters of concentrated hydrochloric acid and allow to stand not more than fifteen minutes. Too long a contact with the acid at this point will cause some of the silicic acid to go into solution. Add hot water, filter the residue through a new, and correspondingly small, filter and wash with hot water.

* Anal. Chemistry (Hall), 2d Ed., Vol. II, p. 445.

† This is sometimes a very tedious operation. Hillebrand says of the drying: "It can safely be done at temperatures higher than that of the water-bath."—*Private communication.*

The amount of silicic acid now remaining in the filtrate should not exceed 0.15 per cent of the total quantity and may usually be neglected. It can be removed, however, by a third evaporation to dryness.

The filters containing the silica are ignited, while wet, in a platinum crucible, and finally over the blast-lamp, and weighed.

Treadwell further remarks: In order to make the separation of silicic acid quantitative, it has been proposed to heat the residue obtained by evaporation at 110°–120° C. It has been found, however, that nothing is gained by this practice, as some silicic acid is obtained in the filtrate and the deposited silicic acid is less pure than when dried on the water-bath. When magnesia was present, more silicic acid was found in the filtrate after igniting at 280° than when dried on the water-bath. This is due to the fact that magnesia formed by hydrolysis reunites with the silica to form magnesium silicate, and the latter is decomposed by hydrochloric acid with the formation of soluble silicic acid. It is, therefore, not advisable to attempt to dehydrate the silica at a temperature higher than that of the water-bath.

20. Peroxide Fusion Method for Silica.—This method is very convenient and frequently serves admirably where other methods, even the carbonate fusion, are unsatisfactory.

Take 0.5 gram of the finely ground material and treat exactly as described in MOLYBDENUM, **1**, up to the point where the crucible has been removed from the melt disintegrated in water. Now transfer the mixture to an evaporating dish of sufficient size, cover the dish and add hydrochloric acid in excess, cautiously, to avoid loss by effervescence. Continue and finish as described in **10**, **11**, and **12**, or according to **19**, which includes two evaporations.

If iron or nickel are to be determined in the same portion as the silica, a nickel crucible may be used in the case of iron and an iron one for nickel; a silver crucible will serve for either. When an iron crucible is employed see that any scales of iron oxide from the crucible are entirely dissolved, before completing the evaporation to dryness, adding more acid if necessary.

Metallurgical products containing carbon, which may be particularly difficult to decompose completely by a carbonate fusion, yield readily to the peroxide fusion; in fact, the method is applicable to almost every case where a fusion is necessary. Always heat slowly

to avoid loss by spattering, or by scintillation due to sulphides or organic matter.

21. Methods in Use at the Colorado Plants of the American Smelting and Refining Co. for the Determination of Insoluble Matter in Ores, etc.*—The methods used in the different laboratories may differ somewhat in unimportant details, but in general are as follows:

Unless there is some special reason for doing otherwise, one-half gram is taken in all cases for the determination.

SULPHIDES

Treat in No. 0 beaker, or small casserole, with strong nitric acid, 7–10 cc. Heat gently until strong action has ceased. Evaporate to dryness and bake until free from acid. Cool, add about 20 cc. hydrochloric acid (1 part acid and 1 part water) and heat until solution is as complete as possible. Filter, wash first with hot dilute hydrochloric acid, then hot water. Ignite and weigh.

Occasionally some ores high in zinc or lead sulphide may be treated to advantage, first with hydrochloric acid, and then as above, but the result should be the same in either case if properly carried out.

OXIDIZED ORES IN GENERAL

Treat with strong hydrochloric acid, 7–10 cc. Boil until dissolved; add a little nitric acid (0.5 cc. is usually plenty); evaporate to dryness and bake to the complete expulsion of acid fumes. Cool; take up with hydrochloric acid and proceed as with sulphides.

With some ores containing carbonaceous matter, it may be necessary to bake for a long time, as such residues often hold acid very tenaciously.

MANGANESE OXIDES

Nitric acid is omitted entirely with these.

LEADY OXIDE ORES

Some of these usually yield gelatinous silica and must be carefully dehydrated at a temperature which is not too high.

OXIDIZED MATERIAL WHICH HAS BEEN STRONGLY IGNITED

Digest with hydrochloric acid without boiling at first, then evaporate nearly to dryness, add a few drops of nitric acid and evaporate

* Western Chemist and Metallurgist, III, 120.

to complete dryness. Occasionally it may be necessary to repeat this treatment, this being a matter of individual judgment. Finally, bake to complete expulsion of acid and proceed as before.

ROASTED ORES, ACID WORKS' RESIDUES, ETC.

Digest with hydrochloric acid, without boiling, until oxidized portion is dissolved, add 2–3 cc. of nitric acid, boil to decompose sulphides, evaporate to dryness and proceed as before.

ORES OR PRODUCTS CONTAINING MAGNETITE

Some mixed oxidized and sulphide ores, and also often furnace mattes, contain magnetite. When this is known or suspected, the material is treated as above under " Roasted Ores, etc.," except that nitric acid in larger quantity may sometimes be necessary.

BARIUM SULPHATE ORES

Treat with 10 cc. hydrochloric acid (1 part acid and 1 part water), boiling a few minutes, add 4–5 cc. nitric acid, and after action has ceased evaporate to dryness. Bake and proceed as usual.

After total insoluble is weighed, fuse with sodium carbonate or mixed carbonates, digest the melt with water until disintegrated, filter and wash. Wash out the fusion crucible with 3–5 cc. hydrochloric acid (1 : 1) and with this dissolve the residue on the filter, being careful that the residue is all dissolved and the filter washed clean. Precipitate the barium in boiling solution with a slight excess of dilute sulphuric acid, and allow to stand at least two hours before filtering. The barium sulphate so obtained is deducted from the total insoluble to give the insoluble residue.

GENERAL NOTES

Care must be taken to insure the removal of all lead salts from the insoluble residue. Filtrations should be conducted rapidly and with hot solutions, in which case washing with hot dilute hydrochloric acid is perfectly safe. However, washing with hot ammonium chloride or acetate solution is often practiced, and there is no objection to it. This removal of lead needs special care in barium sulphate ores, as the latter seem to render the complete solution of the lead salts more difficult.

CHAPTER XXV

SULPHUR

1. Method for Ores, etc., Giving Total Sulphur.—Weigh 0.5 of the finely ground substance. Mix in a small spun-iron crucible (about 25–30 cc. capacity) with 1 gram of dry sodium carbonate and about 5 grams of sodium peroxide. Use peroxide of calorimeter quality, and, after trial, it may be measured instead of weighed. Place the crucible in a hole cut in asbestos board, to prevent absorption of sulphur fumes, and fuse at a gentle heat over a Bunsen burner. Heavy sulphides may require the admixture of more sodium carbonate to prevent deflagration and possible loss.

Set the crucible, while still quite hot in about $\frac{1}{2}$ inch of cold water contained in a 500-cc. beaker. Cover the beaker and upset the crucible with a glass rod. The contents will quickly disintegrate. Remove and wash the crucible. Add about 5 grams of ammonium carbonate to partially destroy the causticity of the peroxide, warm gently until dissolved, and then filter through an 11-cm. filter. A small wad of absorbent cotton, placed in the point of the filter and wetted, will facilitate the filtration. A Witt's plate and suction is a better combination for filtering, and renders unnecessary the use of ammonium carbonate. Wash at least ten times with hot water. Receive the filtrate in a 600-cc. beaker, or transfer to it subsequently. If the filtrate is greenish, indicating manganese, it is a good plan to add 5 cc. of alcohol, boil and then filter again.[1]

2. Add a drop or two of methyl orange as indicator, make just acid with hydrochloric acid and then add 1.2 cc. of the strong acid in excess. Now dilute to 400 cc. with hot water, having previously placed a mark on the beaker at this point.

3. Heat the solution to boiling and add 10–15 cc. of a 10 per cent solution of barium chloride. This is best done through a small funnel supported over the beaker, and having the stem drawn out to a very small opening, so that it will take several minutes to deliver the barium

chloride. Now cover the beaker and boil gently for about twenty minutes, then set aside to settle for an hour or two. This will suffice for ordinary technical work, but in exact analyses the beaker should always be allowed to stand overnight. Filter through a double ashless filter. Unless the filtrate appears perfectly clear, run it through a second time. Wash ten times with hot water. Test the filtrate with a little more barium chloride to be sure precipitation is complete. Transfer the moist filter and precipitate to a weighed porcelain or platinum crucible. Wipe out any precipitate adhering in the funnel with a piece of dry filter paper, and add to the rest. Ignite by first heating very gently until dry, and then at dull redness until the residue is perfectly white. A high temperature, such as that of a blast lamp, is neither necessary nor desirable. Cool in a desiccator and weigh, deducting the weight of the filter ash, or the blank if one has been run.

Multiply the weight of the barium sulphate by 0.1373 to obtain the weight of the sulphur.[2]

It is best to run a blank, once for all, with all the reagents employed, and always deduct for any sulphur thus found. The treatment of the blank should include the fusion in the iron crucible.

In filtering the barium sulphate precipitate, observe the following precaution: after the precipitate has apparently all been transferred to the filter, do not fail to thoroughly rub the inside of the beaker with a "policeman" and a little water, even though the beaker appears perfectly clean. An appreciable amount of sulphate can usually be found.

It is usually unnecessary to test the filtrate from the barium sulphate with more barium chloride, unless the precipitate is large in amount, or the percentage of sulphur found approximates the total quantity that the barium chloride used is capable of precipitating.

Ten cubic centimeters of a 10 per cent solution of barium chloride is the equivalent of 0.1312 gram of sulphur, or, on the basis of 0.5 gram of ore taken, 26.24 per cent.[3] Of course a moderate excess is necessary in order to effect as complete a precipitation as possible. With high percentages of sulphur it is better to start with less ore than to use a large amount of barium chloride. The best excess of hydrochloric acid is 0.3 cc. of the strong acid per 100 cc. of solution.

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[1] Alcohol, being a reducing agent, reduces the higher oxides of manganese in its soluble salts to the insoluble MnO_2, which precipitates.

[2] $BaSO_4$ contains 1 atom of sulphur. Molecular weight of $BaSO_4 = 233.43$. Atomic weight of sulphur = 32.06. 233.43 $BaSO_4 = 32.06$ S; 1 $BaSO_4 = 0.1373$ S.

[3] Crystallized barium chloride has the formula $BaCl_2.2H_2O$. The molecular weight of this is 244.322. Ten cubic centimeters of a 10 per cent solution will contain 1 gram. $BaCl_2.2H_2O$ will precipitate 1 atom of sulphur in forming $BaSO_4$; therefore 244.322 parts by weight = 32.06 parts by weight of sulphur, or, 1 gram = 0.1312 gram of sulphur. On the half-gram basis this = 26.24 per cent.

Additional Notes Relative to Barium Sulphate.—When barium sulphate is precipitated, it tends to occlude other salts in solution, especially ferric iron. This tendency is increased by an excess of hydrochloric acid. Barium sulphate is also appreciably soluble in hydrochloric acid. Hydrochloric acid must, however, be present, and the best results appear to be obtained with an excess of 0.3 cc. per 100 cc. of solution. Ferrous iron causes less contamination than ferric, and while advantage may be taken of this fact; it is usually best to remove iron entirely before precipitation.

Too high a temperature, such as the blast lamp, during the ignition of barium sulphate, may cause a gradual decomposition and loss of sulphur trioxide. A temperature of dull redness is all that is necessary for the ignition.

Another possible source of error is a partial reduction of the sulphate to sulphide by the burning filter-paper. Continued heating with free access of air usually corrects this. Both of these errors may be corrected, after cooling, by adding a drop of sulphuric acid and again igniting carefully. Certain errors due to occluded salts cannot be corrected, and it is therefore best to avoid them, as far as possible, by proper conditions of precipitation.

4. Zinc Oxide Method, Giving Total Sulphur.*—Prepare an intimate mixture of 1 part dry sodium carbonate and 4 parts zinc oxide. Weigh 0.5 gram of the ore into a small platinum or porcelain dish, add 3 grams of the above mixture and mix thoroughly, best by rubbing together with a small agate pestle. Cover with 2 grams more of the zinc oxide mixture. There should always be present at least twice as much sodium carbonate as would be required to combine with the sulphur, arsenic, etc., in the ore. If a platinum dish is used, set it in a hole in a piece of asbestos board (to exclude sulphur coming from the gas), cover partially with a piece of thin asbestos board, and heat over

* The use of the zinc oxide mixture is described by Ebaugh and Sprague, Jour. Am. Chem. Soc., XXIX, 1475.

a Bunsen burner to bright redness, for about twenty minutes. If a porcelain dish is used it is difficult to attain the proper heat with a Bunsen burner, and it is best to heat it in a muffle or over a suitably adjusted blast lamp. Allow to cool and transfer the mass to a 250-cc. beaker. Rinse out the dish well with hot water and make up the bulk in the beaker to about 50 cc. Heat the mixture to boiling, stirring well, and then filter through an 11-cm. filter and wash the residue at least ten times with hot water. Receive the filtrate in a 600-cc. beaker. Add a little methyl orange as indicator, make just acid with hydrochloric acid and then add 1.2 cc. of the strong acid in excess. Dilute the solution to 400 cc. with hot water, heat to boiling and precipitate the sulphur with barium chloride as described in 3.

5. Acid Method for Ores (Not Giving the Sulphur of Barium Sulphate).—Treat 0.5 gram of the ore in an 8-oz. flask with 10 cc. of strong nitric acid. Heat very gently until the red fumes have somewhat abated, and then add potassium chlorate in small portions (say 0.2–0.3 gram at a time), until any free sulphur that has separated is entirely oxidized and dissolved. The acid should not be boiled violently, as this would unnecessarily weaken it. On the other hand, it is best not to allow it simply to simmer, as the explosive gases from the decomposing chlorate may then collect in the flask and produce annoying, although not dangerous, explosions. When the sulphur has entirely disappeared the solution should be boiled to complete dryness. This operation may be hastened by manipulating the flask over a free flame. After cooling, add 5 cc. of strong hydrochloric acid. This should be done cautiously to avoid a too violent reaction with the undecomposed potassium chlorate that may be present. If iron oxide, etc., still remains undissolved, gently heat the hydrochloric acid mixture until solution is as complete as possible, adding more acid if necessary. Finally, boil to dryness, then add 5 cc. more of the hydrochloric acid and again boil to dryness. This is to decompose nitrates and expel all nitric acid. Take up once more in 5 cc. of hydrochloric acid and dilute with about 100 cc. of cold water.* Make alkaline with ammonia and then add 10 cc. of a saturated solution of ammonium carbonate. This latter is to convert any lead sulphate to carbonate and thus render the combined SO_3 soluble, as ammonium sulphate. Heat to boiling, allow the ferric hydroxide, etc., to settle, and then filter

* If the solution is hot when made alkaline with ammonia, some basic ferric sulphate is likely to separate.

and wash very thoroughly with hot water, receiving the filtrate in a 600-cc. beaker. Proceed with the filtrate as described in 2.

6. Modification of the Acid Method for Ores Containing Barium Sulphate.—As barium sulphate remains practically unaffected by the above acid treatment, any sulphur thus combined in an ore will require another method for its solution. When the total sulphur is required in ores containing barium sulphate, the procedure may either be according to 1, or the acid method may be modified as follows: Begin the analysis according to 5, and proceed as described until all nitric acid has been expelled and the residue has been taken up for the last time in 5 cc. of hydrochloric acid. Now dilute with about 30 cc. of water, add 5 grams of pure ammonium chloride and heat to boiling. The ammonium chloride is to hold any lead in solution. Filter and wash with hot water. Reserve the filtrate, which contains all the sulphur that has yielded to the acid treatment. Ignite the insoluble residue, containing the barium sulphate, in a platinum dish or crucible to burn off the filter-paper. When cool, add a little sodium carbonate, or mixed sodium and potassium carbonates, and fuse to decompose the barium sulphate and form soluble alkali sulphate. A prolonged fusion is not necessary. Cool, take up the mass in hot water, warming until thoroughly disintegrated, and then filter and wash with hot water. Make the filtrate slightly acid with hydrochloric acid, keeping the beaker covered to avoid loss by spattering, and then add to it the reserved filtrate. The united filtrates are now cooled (cf. footnote to 5), and made alkaline with ammonia, ammonium carbonate is added, and the determination proceeds in the usual way.

7. Method for Roasted Ores and Ores Containing Much Copper.—By the wet method, some of the sulphur of roasted ores is liable to escape as hydrogen sulphide. Also, if the solution to which ammonia is added contains much copper, some of the latter is liable to separate as a basic sulphate, and, furthermore, the copper in the filtrate will contaminate the barium sulphate. Both of these sources of error may be avoided as follows: Fuse 0.5 gram of the ore in a large porcelain crucible with 25 grams of a mixture of 6 parts sodium carbonate and 1 part potassium chlorate (Böckmann's method). Contamination with sulphur of illuminating-gas is best avoided by placing the crucible within a hole in a piece of asbestos board. Heat gently at first, and finally until the evolution of oxygen ceases. Cool, extract with water

and filter, washing thoroughly with hot water. Acidify the filtrate with hydrochloric acid and continue as described in **2**.

8. Free Sulphur in Ores, etc.—Have the material thoroughly air-dried. Heating to expel moisture is liable to volatilize sulphur. Weigh from 1 to 5 grams, according to amount of free sulphur possibly present. Place in a 200-cc. beaker, add about 30 cc. of aniline and heat the mixture just to the boiling-point for a few minutes, frequently rotating the beaker to stir the contents. Pour the hot liquid through a weighed Gooch crucible with asbestos mat, using suction. Rinse out the beaker several times with carbon disulphide, pouring through the residue in the crucible, until the latter is washed free from aniline. A slight residue remaining in the beaker will soon dry and may be brushed into the crucible. Finally, heat the latter to constant weight at about 100° C. The difference between the final weight of the residue and the original weight of substance taken represents the free sulphur.

Carbon disulphide alone cannot be depended upon to dissolve all the free sulphur, as a modification of the element that is insoluble in carbon disulphide is liable to be present.

It is best to have some water in the receiver under the Gooch filter, both to prevent the hot aniline from cracking the glass, and to prevent the separated sulphur from adhering to the sides.

A possible source of error is water remaining in the substance that might count as free sulphur.

CHAPTER XXVI

TIN

THE following is a rapid and accurate method for the technical determination of tin in ores and similar material. It is a modified combination of ideas from several sources.* The procedure usually requires less than an hour and appears to answer all ordinary purposes.

1. **Oxidized Ores and Similar Material.**—In a thin spun-iron crucible of about 60 cc. capacity, melt about 8 grams of sodium hydroxide (about $2\frac{1}{2}$ inches of the stick hydroxide broken into short pieces). Heat until the moisture is expelled and quiet fusion attained. After cooling, add 0.5 gram of the finely ground ore, cover the crucible with a very loosely fitting porcelain cover and heat, at first cautiously, to lessen spattering, and then with the full flame of a Bunsen burner until the fusion is quiescent. Remove and reserve the cover and pour the melt upon a clean iron plate. Invert an evaporating dish over the hot cake, to prevent loss in case the cake cracks apart violently on cooling.

2. Set the empty crucible in a 400-cc. beaker containing 50 cc. of cold water. Cover the beaker and tip the crucible over with a glass rod, so as to admit the water; then add 40 cc. of strong hydrochloric acid. Warm the mixture and turn the crucible about with the glass rod until it appears clean. Remove and rinse the beaker cover, lift the crucible on the rod and wash off the outside, so as to permit handling with the fingers. Now rinse out the inside of the crucible. If any undissolved melt remains, dissolve it with a little hydrochloric acid and rinse into the beaker. Again cover the beaker and add the cooled melt and porcelain cover. Warm until the cake has dissolved. Lift out the crucible cover with forceps, or by means of a bent iron wire passed through the loop, and wash it.

3. Transfer the solution, which should contain no residue of unde-

* E. V. Pearce, at works of Messrs. Williams, Harvey & Co., Ltd., Cornwall. Ibbotson and Brearly, Analyst, 1902, 25; Technical Methods of Analysis, Griffin.

composed ore (although there may be some scales of iron oxide from the crucible) to a 16-oz. flask. Have this flask prepared as follows: Mark it at the 125-cc. point. Fit a 1-hole rubber stopper in the neck, with a glass tube passing through it a short distance into the flask. Have the tube bent outside at right angles for about 3 inches. Connect this with a flexible rubber delivery tube about 2 feet long, having at the end a short piece of glass tubing drawn to a tip with an opening of about a millimeter. See Fig. 18.

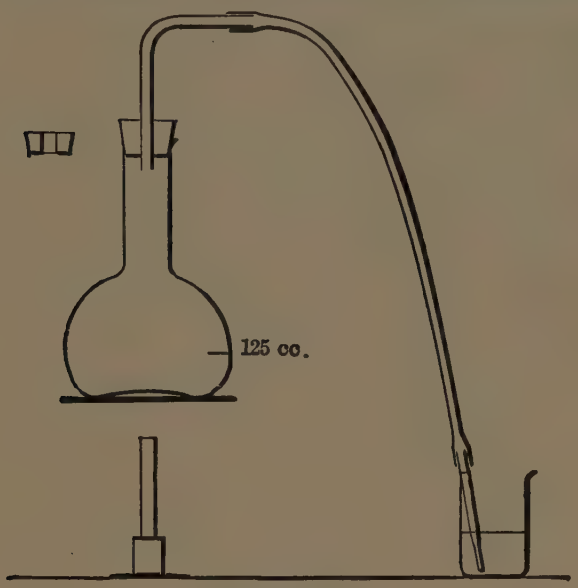

FIG. 18.

Also have ready about 100 cc. of a 10 per cent solution of sodium carbonate.

4. Bring the solution in the flask to the 125-cc. point by dilution or boiling, as necessary. Remove from the heat if boiling was required. Add about 0.5 gram of finely powdered metallic antimony * and 40 cc. of strong hydrochloric acid. Insert the stopper, again place over the heat and dip the glass tip of the delivery tube into a small beaker containing about 40 cc. of the sodium carbonate solution. Now lift the stopper of the flask slightly, pour in 25 cc. of the sodium carbonate solution and again close the flask.

5. Heat to boiling and then lower the flame so as to produce a very gentle boiling. Maintain at this temperature for fifteen minutes; by this time all the tin should be reduced to the stannous condition. Keeping the glass delivery tip continually at the bottom of the small beaker, cool the flask and contents completely, to room temperature or cooler, under the tap.

6. Remove the stopper without unnecessary agitation of the flask, and immediately slip in its place a rubber stopper cut very short ($\frac{3}{8}$ in.), having a hole slightly larger than the delivery tube of the burette to be used. Add about 5 cc. of starch solution, by means of a 10-cc. pipette inserted through the stopper with the tip reaching nearly to the liquid. See that there is no air in the tip of the pipette and do not allow all the starch solution to run out, as this would draw in air.

* This is easily prepared by grinding a little crushed antimony in a wedgwood mortar.

7. Insert the delivery tube of a burette filled with standard iodine solution, through the hole, well into the flask, and titrate to a faint, permanent blue tinge. Rotate the flask gently after each addition of iodine and do not withdraw the burette tip during the titration.

Multiply the number of cubic centimeters of iodine solution used, by the percentage value of 1 cc., to obtain the per cent of tin.

None of the ordinary constituents of tin ores interfere with this method. Both arsenic and antimony in the *ous* condition in weak acid solution consume iodine, but in a solution containing at least one-fifth of its volume of strong hydrochloric acid they are entirely without effect.

Notwithstanding the above statement, it is always best to run a blank with the antimony used. Weigh 0.5 gram into the same flask used for the tin. Add 125 cc. of water and 50 cc. of strong hydrochloric acid, and conduct the procedure from this point precisely as described for tin. Deduct the amount of iodine solution required to produce a blue tinge from the cubic centimeters used in the tin assay, before calculating the latter.

8. The standard iodine solution may be prepared by dissolving about 11 grams of iodine in a little water with the addition of about 20 grams of potassium iodide, and diluting to 1 liter. On the basis of 0.5 gram of ore taken for assay, 1 cc. will equal about 1 per cent of tin.

Standardize as follows: Weigh carefully about 0.2 gram of pure powdered arsenious oxide into an 8-oz. flask. Dissolve by warming with a little dilute sodium hydroxide solution. When dissolved, dilute to about 100 cc. with cold water, add a few drops of phenolphthalein solution as indicator and make slightly acid with hydrochloric acid. Now cool under the tap to room temperature or cooler. Finally, add 3–4 grams of sodium acid carbonate and a little starch solution * and titrate to a permanent blue color with the iodine solution. The weight of the As_2O_3 multiplied by 1.199 equals the weight of the equivalent amount of tin.[1] Having determined this weight in grams, change it to per cent (on the basis of 0.5 gram = 100 per cent), by multiplying by 2 and moving the decimal point two places to the right. This figure, divided by the number of cubic centimeters of iodine solution used, will give the percentage value of 1 cc.

The iodine solution does not change materially in a week, but it is not safe to use a standard that is older.

* If an acid starch solution is used add it before neutralizing.

9. Sulphide ores should be oxidized before the fusion. As roasting might cause loss, it is best to treat with aqua regia until the sulphides are decomposed, then dilute, filter off the tin oxide and gangue and ignite this residue in a porcelain crucible at a low heat (it is unnecessary to burn off all the carbon) and proceed with it as described above.

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[1] When tin is oxidized from the stannous to the stannic condition it amounts to the same as changing SnO to SnO_2 by the addition of 1 atom of oxygen. Every Sn then, =O. When As_2O_3 is oxidized to As_2O_5, every As_2O_3 requires O_2, or, $As_2O_3 = Sn_2$. Molecular weight of $As_2O_3 = 197.92 = 237.4$ Sn, or, 1 $As_2O_3 = 1.199$ Sn.

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10. **Method of E. V. Pearce for the Determination of Tin in Ores, etc.**—Fuse * 8–10 grams of stick sodium hydroxide in a $2\frac{1}{4}$-inch nickel dish with the addition of a sprinkling of finely powdered charcoal, keeping the dish covered with a porcelain crucible-cover. When the sodium hydroxide is thoroughly fused, remove the lamp and allow to cool slightly.

11. Weigh from 0.2 to 0.5 gram, according to its supposed richness, of the finely powdered ore, place it in a thin layer over the cooled melt in the dish, and sprinkle a little more charcoal over the ore. Cover the dish and heat again, cautiously at first to avoid spattering, finally with the full power of a Bunsen burner for five or ten minutes, or until no further action is seen. Allow to cool; when cold the separation of the cake may be effected by squeezing the dish in the hand. Transfer the cake to an evaporating-dish (a glazed iron dish is ordinarily employed), add water, and thoroughly clean and wash the nickel dish and cover. Now cover the evaporating-dish and add sufficient strong hydrochloric acid to effect a complete solution of the cake, with the exception, possibly, of some gelatinous silica. Under ordinary circumstances the latter may be disregarded, but, if desired, it may be removed by filtering through glass wool. Transfer the solution to a

* For this description I am indebted to Dr. Richard Pearce, who has kindly written it with the consent of Mr. E. V. Pearce, his nephew. Dr. Pearce describes the method as he has seen it in daily use at the works of Messrs. Williams, Harvey & Co., Ltd., in Cornwall, with which his nephew is connected. In regard to its accuracy, Dr. Pearce states: "I have seen the method tried on various ores and mixtures, the latter being prepared with percentages of tin known only to myself, and am quite satisfied with its accuracy and rapidity. In my opinion it is far ahead of any method which has yet been suggested for the assay of tin, especially in low grade ores."

tall narrow beaker, add a few rods of iron (nail-rod),* about 3 or 4 inches long, cover the beaker and warm it gently to effect a free evolution of hydrogen. The ferric chloride is reduced to a ferrous salt, the yellow color giving place to a pale green, and then the stannic chloride is reduced to stannous chloride. The whole reduction is complete in thirty minutes or even less. Now place the beaker and contents in a dish in which cold water is circulating, until the solution is as cold as possible. Remove and wash the iron rods, add a little starch liquor, and the solution is then ready for titration with a standard iodine solution.

12. The latter is prepared in the usual way by dissolving iodine in a solution of potassium iodide, and is standardized with pure tin or pure arsenious oxide. About a N/10 strength is convenient.

13. In the case of ores containing pyrites, the latter should be oxidized before the fusion. To avoid possible loss in roasting, it is best to treat with aqua regia until the sulphides are decomposed, then dilute, filter, and ignite the residue, containing all the tin oxide, at a low temperature in a porcelain capsule (it being unnecessary to burn off all the carbon) and proceed with it as described above.

14. In regard to his method, Mr. E. V. Pearce writes: "I should explain to you that the merit of my process lies in the ease with which the tin is obtained in solution. The titration with iodine which I am using has been elaborated by L. Parry and is described in detail in his book, 'The Assay of Tin and Antimony.' The advantages of the process, in conjunction with the iodine titration over any other known tin assay are:

"1. The ease with which all the tin is obtained in solution;

"2. The absence of any filtrations;

"3. No separation of other metals is necessary;

"4. The speed with which an assay can be made,—1½ hours being sufficient for any ores."

NOTE.—Mr. E. V. Pearce has recently called my attention to the fact that the omission of charcoal in the decomposition, according to my modification of his method, is apparently permitted by the use of an iron crucible. When a nickel crucible is used, the decomposition is frequently incomplete if charcoal is omitted, but iron filings appear to serve equally as well as charcoal. The iron of the crucible is therefore a factor in the reactions, and Mr. Pearce prefers the method I describe, as being more convenient than the use of either charcoal or iron filings. The weak point of this method is the likelihood of the stannous solution being oxidized by the air during titration, causing a low result.

* Mr. Pearce now uses sheet nickel as the reducing agent. I have likewise found nickel preferable to iron.

15. Parry's Method for the Assay of Tin Ore.*—Tin ores may be either pyritic or non-pyritic. Pyritic ores holding more than two per cent sulphur must be, and non-pyritic ores may be, treated with nitric acid before reduction, as tin sulphide is volatile at a red heat. Weigh 5 grams of the ore, ground as finely as possible, either directly into a porcelain boat, or treat in an evaporating dish with a watch-glass cover, with 20 cc. of dilute nitric acid, and carefully evaporate to complete dryness. Digest the residue with dilute nitric acid and filter. Dry the washed residue, ignite it in the dish, and then transfer it to a porcelain boat and heat it to low redness for two hours, in a slow current of hydrogen or coal gas. Coal gas is much more convenient to use and quite as effective as hydrogen. The boat is $2\frac{1}{2}$ by $\frac{1}{2}$ in., and two at a time may be placed in a porcelain or glass tube 12 in. long, with a $\frac{3}{4}$ in. bore, which is then placed in the reduction furnace. A very convenient form of gas reduction furnace, with clay body, brass gas jets, and asbestos rings to fit over the ends of the tube

Fig. 19.

against the clay covers, is made in 6-in. lengths. The ends of the tube should project about 3 in. at each end of the furnace, and should be closed with rubber stoppers fitted with glass tubes as shown; the escaping gas (about 4 bubbles per second) is passed through dilute hydrochloric acid, in which any volatilized tin is condensed. In ores holding not more than 2 per cent sulphur—that is to say, in 99 out of 100 samples of black tin or tin barilla, as bought, treatment with nitric acid may be omitted. In these direct reduction assays the tube is washed out, after the reduction is complete, with hydrochloric acid and potassium chlorate, also the glass leading tube. The solution is mixed with that through which the gas bubbled, reduced with iron and titrated for tin with iodine. This generally adds 0.1 to 0.2 per cent on the main tin assay. Where treatment of the ore with nitric acid is adopted as a method, the tube may still be similarly washed out, and, together with the gas liquor, tested for tin, as a check, for

* L. Parry, London Mining Jour., Sept. 25, 1909; also Parry's "The Assay of Tin and Antimony."

instance, against volatilization of tin on account of sulphur in the gas. A two-way gas branch is used; one jet supplies gas to the tube, the other supplies gas for heating the furnace. After the reduction, allow the boats to cool in the furnace, and, when cold, transfer each boat and its contents to a 400-cc. beaker and treat with 150 cc. of hydrochloric acid and 5 cc. of nitric acid. Allow the assay to stand in a warm place until the action abates, then boil for a few minutes, dilute with an equal bulk of water and filter. Wash the residue well with hot acid water, then with hot water, and then dry and ignite it. Fuse the ignited residue with 4 or 5 parts of a mixture of sodium carbonate (free from chlorine) and borax, in a platinum crucible. Dissolve the melt in hydrochloric acid and precipitate with zinc, as usual. The residue rarely holds more than 0.5 per cent of the total tin in the ore. Instead of being fused as above, the residue may be fused with about 2 in. of stick sodium hydroxide in an iron crucible over a Bunsen burner. Dissolve the melt in hydrochloric acid and precipitate on zinc as usual. Make up the main solution to 500 cc., pipette off the equivalent of 1 gram into an 8-oz. flask, reduce with iron wire and filter. Precipitate the filtrate with strips of sheet zinc as usual. Dissolve the metallic sponge in hydrochloric acid and titrate at the boiling-point with standard ferric chloride solution.

In precipitating the tin with zinc, neutralize the solution (which should be freely acid) with thin strips of zinc. Use an excess of zinc at the beginning, as, if the neutralization is effected too slowly, tin is apt to remain unprecipitated. When the action ceases pour a little of the liquor into a beaker containing some hydrogen sulphide water; if the precipitate is white all the tin has been thrown down. Pour away the mother liquor as closely as possible, after allowing any floating particles of metal to settle. The best plan is to pour the liquid from the flask into a beaker, which is then rapidly filled with water from the tap. Press the larger pieces of spongy tin against the side of the beaker with a glass rod, after which they will readily settle. The addition of a drop or two of ammonia, or pouring the liquid to and fro from one beaker to another, will generally insure the settling of the lighter particles. Wash the metal in the beaker back into the flask with 180–200 cc. of hydrochloric acid, to dissolve the tin and zinc, and bring the liquid to a boil as rapidly as possible, with the addition of a granule of zinc. The flask should be provided with a rubber stopper through which passes a short length of glass tubing.

If the acid is not brought to a boil rapidly, the metal may be completely dissolved while there is still air in the flask, and some stannic chloride may be formed. When the solution is complete, and the liquid boiling, titrate at once with ferric chloride. One drop of the ferric chloride solution in excess should produce a plain yellow tinge. The end-point is more marked the hotter and more acid the solution.

Under ordinary circumstances it is better to let the action cease completely when precipitating with the zinc, but in the rare cases when titanium is present (as evidenced by the violet color of the solution during the precipitation), the liquor must be poured off from the tin and zinc while it is still slightly acid, all the titanium being then in solution as sesquichloride. Also, the sponge of tin and zinc should be washed once with water slightly acidulated with hydrochloric acid. Under these circumstances no titanium hydroxide is left with the tin and zinc. Ti_2Cl_4 is oxidized by ferric chloride, though it is unaffected by iodine. In the case of an insoluble silicious residue from solution (after gas reduction) of an ore, which is apparently poor in tin and rich in titanium, it would be a convenient plan, after fusing and dissolving in hydrochloric acid, to reduce the solution with iron and titrate with iodine, instead of precipitating with zinc for the ferric chloride assay, as the silicic acid sometimes deposited from hydrochloric acid solutions during zinc precipitation may carry down titanic acid with it or occlude titanous chloride mechanically. If, however, any titanium got through into the hydrochloric acid solution for ferric chloride titration, its presence would at once be shown by the color. On rich material the ferric chloride titration should be employed whenever possible, as the iodine titration, even under the best conditions, has a slight tendency to give low results.

16. *Preparation and Standardization of the Ferric Chloride Solution.*—The ferric chloride solution should be made up 2 liters at a time, from a concentrated stock solution made by dissolving piano wire in hydrochloric acid, peroxidizing with nitric acid and evaporating twice with hydrochloric acid to dryness, and then dissolving in hydrochloric acid. It is standardized against 1 gram of the purest tin, filed with a fine file. The ferric chloride solution may also be made by dissolving 180 grams of the yellow commercial lump salt, which is roughly $Fe_2Cl_6.12H_2O$, in about 200 cc. of hydrochloric acid and evaporating to dryness. The residue is dissolved in 300 cc. of hydrochloric acid and diluted to 2 liters. The evaporation is to free the

solution from nitric acid and arsenic. Use only the purest and strongest hydrochloric acid.

To standardize, weigh 1 gram of pure, finely divided tin into an 8-oz. flask, add strong hydrochloric acid until the flask is about three-fourths full, insert a rubber stopper provided with a few inches of small glass tubing, and boil the mixture until solution is complete. Do not boil too rapidly, as this weakens the hydrochloric acid too much before the tin is dissolved. Neither should the liquid come to a boil too slowly, as all the tin might then be dissolved before the air in the flask was thoroughly expelled, and stannic chloride might be formed. When solution is complete, titrate the boiling-hot solution at once. Use a fast-running burette with a glass stopcock. Two or three minutes' delay in titrating will not show a perceptible effect, but after five minutes, oxidation is apparent and increases rapidly. The end-point of the titration is indicated by a yellow tinge, which is produced by an excess of 1 drop of the ferric chloride solution. If the liquid in the flask turns dark greenish after the titration, the ferric chloride is contaminated with nitric acid. One cubic centimeter should equal about 2 per cent of tin, on the basis of 1 gram taken for assay.

In the assays, the main portion of the titration must be done with the above ferric chloride solution, but it may be finished with a solution of half or quarter strength, in order to obtain a more exact ending.

Notes.—Any copper in the tin ore is found in the nitric acid solution, though traces may remain with the SnO_2. In the iron wire stage, the arsenic which escaped extraction with nitric acid and volatilization in the reduction tube, is partly evolved as AsH_3 and partly precipitated with antimony in the metallic form. It comes down as a brown flocculent deposit, which contains 3 or 4 per cent of its weight in tin. As there is generally only 1 or 2 per cent at most, and usually under 0.5 per cent, of arsenic in a tin ore, the loss of tin from this cause is quite negligible, but as a check one should save the iron wire and precipitates and filter-papers, and examine them from time to time for tin. It will be found, as in the case of the deposit in the tube, and the dilute hydrochloric acid through which the escaping gas bubbles, that only the merest traces of tin are lost in these operations. Further, one may make the hydrochloric acid solution of the reduced metal in a conical flask with a rubber stopper and tube dipping under water,

to assure oneself that there is no appreciable loss by volatilization of $SnCl_2$.

If the ore contains tungsten it is mostly found as WO_3 in the residue from the hydrochloric acid and nitric acid extraction of the reduced metal, from which it may be removed, before fusion, with ammonia. Any tungsten which gets into the main solution comes down as blue oxide with the iron wire precipitate, and any which is fused with sodium carbonate and borax should be removed by reducing the hydrochloric acid extract of the melt with iron wire before precipitating with zinc. In general, all the antimony and some of the lead in the ore will be found in the main hydrochloric acid solution, while some of the lead will be obtained in the nitric acid extract.

After the nitric acid evaporation the residue may be boiled with hydrochloric acid (about 50 cc.), diluted and filtered, though in this case the extract must be tried for tin as a matter of precaution. It will, in general, hold all the copper and most of the arsenic, antimony, lead and iron, though one can never be sure that the residue is free from the oxides of these metals. Occasionally this hydrochloric acid extract will hold a little tin. The residue is reduced in the usual manner.

Except with impure ores, the reduction with iron wire may be omitted, as it is always an advantage to save a filtration when possible, and as the small amount of antimony usually present is evolved as stibine during the zinc precipitation. In this case the aliquot part of the solution is at once precipitated with zinc. The boiling hydrochloric acid solution for titration with ferric chloride must, however, be free from black powder of Cu, Sb, etc., and from tungsten blue in suspension or solution. (Lower oxides of tungsten in solution give a brownish pink or light claret colored solution.) During precipitation with zinc the solution should be freely acid to start with, and in the presence of Ti or Mo should be distinctly acid when poured off, as titanium and molybdenum interfere with the ferric chloride titration, titanium sesquichloride reducing ferric chloride.

When copper, or appreciable amounts of antimony, or arsenic, or bismuth are present, reduction from iron must precede zinc precipitation. Instead of doing this with iron wire in a flask, use a 400-cc. beaker (tall shape), and one strip of sheet-iron about $\frac{1}{2}$-in. in width, and of sufficient length to leave about 1 in. above the surface of the liquid. This will be easy to wash. The assay must be filtered hot,

and the paper thoroughly but rapidly washed with hot water strongly acid with hydrochloric acid. Under the assay conditions, the residue is free from tin. After zinc precipitation, care must be taken to insure that no floating particles of metal are poured off with the mother liquor, or left in the beaker after redissolving in hydrochloric acid. The mother liquor must always be tested with hydrogen sulphide. The assay for titration is brought to a boil as rapidly as possible, and should begin to boil before all the metal is in solution. The addition of a granule of zinc effects this. The zinc used in precipitation must be good thin sheet-zinc, free from tin.

CHAPTER XXVII

TITANIUM

1. Gravimetric Determination: Gooch Method, Modified.*—This method is applicable to minerals and metallurgical products that are comparatively high in titanium. The method provides for the separation of titanium from iron, aluminum and phosphoric acid, with which it commonly occurs. The procedure, as proposed by F. A. Gooch and modified for non-aluminous rocks by Wm. M. Thornton, has been found by Scott to give reliable results. The details of the method, with a few slight changes found to be advantageous, are given below. Iron is separated from titanium by precipitation as a sulphide in the presence of tartaric acid; the organic acid is destroyed by oxidation and the titanium precipitated from a boiling acetic acid solution. In the presence of alumina and phosphoric acid the impure precipitate is fused with sodium carbonate and the impurities leached out with boiling water.

2. Procedure.—*Ores High in Silica.*—Treat 1 gram or more in a platinum dish with a mixture of 10–15 cc. of 50 per cent hydrofluoric acid and 3–4 cc. of strong sulphuric acid per gram of sample.

Oxides.—Decompose by fusion with sodium or potassium acid sulphate.

3. The decomposed mixture, however obtained, should not contain over 0.2 gram of titanium. Take it up in 10 per cent sulphuric acid, keeping the volume as small as possible.

Precipitation of the Iron.—Add tartaric acid equal to three times the weight of the oxides of titanium to be held in solution. The amount in any case should not exceed 1 gram, as the subsequent removal of larger quantities would be troublesome.

Pass hydrogen sulphide into the solution to reduce the iron, then add ammonia to slight alkalinity, and again pass in hydrogen sulphide to completely precipitate FeS. Filter, washing the ferrous sulphide

*W. W. Scott's "Standard Methods of Chemical Analysis."

with very dilute colorless ammonium sulphide. The titanium in the filtrate is entirely iron-free.

Oxidation of the Tartaric Acid.—The tartaric acid must be removed, since titanium cannot be precipitated by any reagent in its presence. Transfer the filtrate to a 500-cc. Kjeldahl flask, add 15–20 cc. of strong sulphuric acid and boil until incipient charring occurs. Cool slightly, add about 10 cc. of fuming nitric acid, very cautiously, a few drops at a time, and when the first violent action has subsided heat the flask gradually (under a hood). A vigorous reaction will take place, accompanied by much effervescence and foaming, with evolution of copious brown fumes. The organic matter will gradually disappear, the effervescence becoming steady and finally ceasing, and white fumes of SO_3 will appear. Cool the solution and pour the pale yellow syrup into 100 cc. of cold water. Wash out the flask, adding to the rest. Filter the solution if it is cloudy.

Precipitation of the Titanium.—Add ammonia until the solution is nearly neutral. This point may be recognized by the production of a slight turbidity, which clears by vigorous stirring. If a trace of iron is suspected, add about 1 cc. of a 10 per cent solution of ammonium acid sulphite. Now add 5 cc. of glacial acetic acid, then 15 grams of ammonium acetate, and make up the volume of the solution to about 350 cc. Heat rapidly to boiling and maintain in ebullition for about three minutes. The titanium will precipitate in a white flocculent and readily filterable condition. Filter off the precipitate, washing first with water containing acetic acid and finally with pure water. Ignite filter and precipitate, at first cautiously over a low flame, and then intensely for twenty minutes. Weigh the residue as TiO_2.

In the presence of large amounts of alumina and phosphoric acid, fuse the residue with sodium carbonate in a platinum dish. Leach the melt, after cooling, by boiling with pure water. Alumina and phosphoric acid go into solution as soluble sodium salts, while titanium oxide remains insoluble in the residue.

Ignite the insoluble residue and weigh as TiO_2.

4. Colorimetric Method for Iron Ores.*—Take 0.1 gram of the finely powdered mineral and mix it in a platinum crucible with 0.2 gram of sodium fluoride, also finely powdered. Add 3 grams of sodium pyrosulphate, without mixing. Fuse carefully, holding the burner in the hand. Heat gently till the effervescence ceases and copious

* Method of W. A. Noyes, Jour. of Anal. and Appl. Chem., V, 39.

fumes of sulphuric acid are evolved. This takes only two or three minutes. When cold, dissolve the mass in the crucible in 15 to 20 cc. of cold water and filter the solution. The filtrate and washings need not exceed 20 cc. If a residue remains, it can be treated again by the same method, after burning the filter, but the amount of titanium found by a second fusion is usually very small.

To the solution add 1 cc. of hydrogen peroxide and a few cubic centimeters of dilute sulphuric acid, and compare the color (orange red to yellow) with that of solutions containing known amounts of titanium. Nessler tubes may be used for this purpose, and the solutions are all brought to the same volume, say 30 or 50 cc. For a standard solution, dissolve titanic oxide in hot concentrated sulphuric acid and dilute the solution till 1 cc. contains 1 mg. of TiO_2. In diluting it is best to use dilute sulphuric acid at first, to prevent the precipitation of titanic oxide.*

The colors produced are more or less affected by the presence of iron, and it is therefore advisable to add to the comparison-tubes an amount of ferric sulphate corresponding approximately to that in the solution which is being tested. A solution of ferric ammonium alum answers well for this purpose, and all that is necessary is to match the color of the solution of the mineral before adding hydrogen peroxide to it. If this is done, titanium can be readily determined in the presence of very considerable amounts of iron. Thus, 0.02 mg. of titanic oxide can be detected in 30 cc. of water in the presence of 0.1 gram of ferric oxide in the form of sulphate. This would correspond to 0.02 per cent for 0.1 gram of mineral.

Determinations based on a comparison of tints are especially valuable for the estimation of small quantities of elements, and for most cases where titanium requires determination the above method is amply accurate. It works excellently with magnetite and other iron ores. There appears to be no appreciable error caused by the volatilization of titanium as fluoride.

5. Test for Titanium.—A qualitative test for titanium can be made in five minutes as follows: Mix a little of the powdered ore with sodium fluoride, add sodium pyrosulphate, and fuse as above. Cool by dipping the crucible in cold water. Add 2 or 3 cc. of dilute sulphuric acid and 10 cc. of water. Dissolve by boiling. Divide the solution in two portions, and to one add a few drops of hydrogen

*See 6.

peroxide. A comparison with the solution to which no hydrogen peroxide has been added will show at once whether titanium is present or not.

6. Preparation of Standard Solution of Titanic Oxide.—I have found difficulty in preparing a standard solution of titanium by dissolving titanic oxide in hot concentrated sulphuric acid. The following method is satisfactory:

Ignite pure titanic acid until all water of hydration is expelled. Weigh 0.5 gram into an 8-oz. flask, add 10 cc. of strong sulphuric acid and 5 grams of potassium sulphate. Heat over a free flame until the titanic acid is dissolved and the solution is clear. Cool, dilute with 125 cc. of 1 : 4 sulphuric acid, transfer to a 500-cc. measuring flask and make up to the mark with cold water. When perfectly cool, again adjust to the mark and mix thoroughly. One cubic centimeter will contain 1 mg. of TiO_2. A more accurate method of preparing this standard solution may be found in Bulletin No. 305 of the U. S. Geological Survey, p. 111.

7. Notes on Colorimetric Method.—The color produced by titanium is destroyed by hydrofluoric acid or fluorides. Vanadium produces a very similar color, which, however, is not thus destroyed. Another method of distinguishing between the two elements in the qualitative test is as follows: Divide the solution in two test-tubes. Add to one 5 cc. of water and to the other 5 cc. of 3 per cent hydrogen peroxide solution. If titanium alone is present the peroxide tube will show a yellow or orange-yellow tinge when compared with the other. A distinctly reddish tinge indicates vanadium, with titanium also possibly present. Add 1/20 N ferrous sulphate solution, 1 cc. at a time, shaking after each addition. The red color will gradually fade. If it fades to a yellow, titanium is present, otherwise it will fade out without changing to yellow.

CHAPTER XXVIII

TUNGSTEN

1. Method for Ores.—Weigh 0.5 gram of the very finely ground ore into an 8-oz. flask ("copper-flask"). Add 3 grams of anhydrous sodium sulphate and 5 cc. of strong sulphuric acid. Heat over a free flame, preferably with the flask in a holder, until the free acid is all expelled and the mixture reduced to a red-hot melt. Continue the fusion until the decomposition is complete. By holding the flask at an angle, so that most of the heat is on the curve just above the bottom, the latter is prevented from bulging. Give the flask a slight circular motion during the heating. Rotate it while cooling, so as to distribute the melt around the sides, and thus avoid cracking. The decomposition is usually very quickly effected without any material injury to the flask. A Pyrex flask is to be preferred.

2. When the melt is cool, add 20 cc. of hot water, 20 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid. Boil until the bulk is reduced to about 10 cc. Add 25 cc. of hot water, and 3 cc. of cinchonine solution, and cool under the tap, to room temperature or cooler.

The cinchonine solution is made by dissolving 25 grams of cinchonine in 200 cc. of 1 : 1 hydrochloric acid.

3. Filter the cold mixture through a 9-cm. filter, returning the first portion if at all cloudy. The flask may be washed out with cold water while the filter still contains liquid, if the washing is done quickly. It must be remembered, however, that cold water alone, with no cinchonine present, will soon cause a cloudy filtrate. Wash filter and precipitate twice with dilute cinchonine solution (5 cc. of the above solution diluted to 100 cc.) contained in a small wash-bottle. The flask may retain a little WO_3 adhering to the sides.

4. Spread the filter carefully on a watch-glass and wash the precipitate, through a funnel, back into the flask with hot water, using as

little as possible. Pour about 1 cc. of ammonia upon the filter in the watch-glass and set the whole on a water-bath to dry.

Add 1 gram of sodium carbonate to the mixture in the flask and boil to small bulk while the filter is drying. Re-fold the dry filter in the original creases and replace in the funnel. Rub up any adhering residue on the watch-glass with a little water and wash through the filter into a clean flask like the first. Pour the concentrated liquid in the original flask through the filter and wash out the flask with hot water. Now pour a little ammonia into the washed flask, add about 50 cc. of hot water, and use this solution to wash the filter at least ten times, with about 5 cc. each time.

5. Boil the filtrate to small bulk. This will expel all the ammonia. Add 2 grams of anhydrous sodium sulphate and (cautiously) 5 cc. of strong sulphuric acid. Spattering may be avoided by first cooling under the tap. Boil the mixture in the flask in the original manner, as described in 1, until the free acid is expelled and any carbon from the cinchonine is burned off. Cool as before, add 20 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid, and boil down to about 10 cc.

Add 25 cc. of hot water, and 3 cc. of cinchonine solution, and cool and filter as before, using an 11-cm. ashless filter. Before washing the filter, pour a little ammonia into the flask to dissolve adhering WO_3, and boil the solution until all free ammonia is expelled. Now add a few drops of hydrochloric acid and about 1 cc. of the dilute cinchonone solution, and cool under the tap. Pour the cold mixture into the filter and wash out the flask quickly with cold water. Wash filter and precipitate at least ten times with the cold dilute cinchonine solution.

6. Transfer the washed filter and precipitate to a small weighed platinum dish and ignite until the carbon is burned off. Cool, add a few cubic centimeters of hydrofluoric acid and evaporate to dryness to remove any silica. Again ignite and then cool and weigh as WO_3. Multiply the centigrams by 2 to obtain the per cent.

Note.—Quinine may be substituted for cinchonine, if desired.

Tungsten in ores is usually reported as the oxide, WO_3, instead of the element. Most of the methods described for its determination are very tedious, either in the original decomposition of the ore or in the subsequent operations. In the majority of cases the above method is both rapid and accurate. The decomposition of the ore may sometimes be varied with advantage, by the addition of a little hydro-

fluoric acid (1 cc.), to attack silica, or a small piece of filter paper to act as a reducing agent, or both. These additions are usually quite unnecessary.

7. Hydrofluoric Acid Method for Ores.—Treat 0.5 gram of the very finely powdered ore in a small platinum dish with equal parts of strong hydrochloric and hydrofluoric acids. Digest on a water-bath until solution is complete, adding more of each acid from time to time if necessary. It may require from one to several hours to effect complete decomposition of the ore. Usually a perfect solution may be obtained. Any tin oxide present will be unaffected. Finally, evaporate to about 15 cc. with an excess of hydrochloric acid. A yellow precipitate of H_2WO_4 may separate during the final evaporation, owing to the expulsion of the hydrofluoric acid that holds it in solution.

8. Transfer the solution and any precipitate to an 8-oz. flask. If some of the precipitate adheres to the dish, remove as much as possible with a rubber-tipped glass rod and rinse into the flask with a very little hot water. If some still remains, pour a few cubic centimeters of strong ammonia over it, cover the dish and set it aside for the time being.

To the mixture in the flask add 20 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid. Boil down to about 10 cc. This will expel any remaining hydrofluoric acid and precipitate the tungsten as tungstic acid, H_2WO_4. Dilute with 50 cc. of hot water and allow to simmer at a gentle heat for about half an hour, or until the tungstic acid has settled clear. Filter, washing well with hot water.

9. The tungstic acid on the filter is now to be dissolved with warm dilute ammonia and the filtrate evaporated to dryness in a weighed platinum dish. Use the same dish as before. If it already contains ammonia, added to dissolve adhering tungstic acid, see that the latter has all dissolved, warming if necessary, and then rinse the solution into a small beaker. Dry, ignite and weigh the dish and place it under the funnel. Warm the ammoniacal solution in the beaker and pour it over the precipitate in the funnel. Continue to pour on more warm dilute ammonia, very slowly, so as to use as little as possible, until the precipitate is all dissolved, washing the filter with the same solution.

Evaporate the filtrate in the platinum dish on a water-bath, to dryness, and then ignite the residue at a red heat. Cool and weigh as WO_3. Multiply the weight in centigrams by 2 to obtain the per cent. If tungsten is desired, $WO_3 \times 0.793 = W$.

The cold residue should be of a bright canary-yellow color.

10. Watts' Method for Ores.*—This is a very good method, but it has the disadvantage of requiring a long time for the decomposition of the ore. The ore must be in the finest possible state of division. The time spent in grinding will be more than made up for later. Laboratories using the method regularly, employ a large agate mortar with pestle specially fitted to run by power.

Usually 1 gram of the agate-ground sample is taken for analysis, whatever the grade, except in the case of extremely low-grade ores or tailings, when 2 grams are taken.

The method of attack by acid depends somewhat on the grade of the ore; if not over 30 per cent it is treated directly by evaporating with about 40 cc. of aqua-regia; if much above this, and always in the case of concentrates, the assay is started with 40 to 50 cc. of hydrochloric acid alone. In the latter case, when the solution has evaporated to say, 15 cc., about 25 cc. of aqua-regia are added and the evaporation again carried on until the solution has evaporated to 15 cc. The evaporation is conducted in a small covered beaker on a hot-plate.

The beaker is now removed from the hot-plate, 50 cc. of hot water are added and the mixture is allowed to stand for twenty or thirty minutes. The nearly clear solution is now decanted through a filter, as much of the residue as possible being kept in the beaker. The residue is now washed twice by decantation; 50 cc. of hot water, containing a little hydrochloric acid, are used each time.

To the residue in the beaker add about 15 cc. of ammonia solution (made by adding 400 cc. of strong ammonia to 2000 cc. of water containing 20 cc. of strong hydrochloric acid). Warm slightly until all the liberated tungstic acid is in solution. Decant through the original filter, receiving the filtrate in a large porcelain crucible. (If the ore is low grade, platinum should always be used.) The residue is now examined for any undecomposed particles of mineral; if none are found, transfer the whole to the filter with the ammonia solution (used warm in a wash-bottle). The filter is then further washed with the same solution until free from tungstic acid. Five washings of 2 or 3 cc. each will suffice, if the stream is directed around the top of the filter.

Should any undecomposed mineral be found after the first treatment with ammonia, as may sometimes be the case owing to the pro-

* Communicated by Hugh F. Watts, Boulder, Colo.

tective action of the liberated tungstic acid, wash three times by decantation with ammonia solution and then, instead of transferring to the filter, again treat with aqua-regia, which should not be stinted in amount, even if the residue is small. Use at least 30 cc. and treat exactly as at first, except that smaller amounts of wash solutions will suffice. The tungstic acid liberated by the second acid treatment is apparently somewhat more difficultly soluble in ammonia than the first obtained, but warming and stirring will finally cause it to dissolve. Add this solution to the main ammonia solution in the large porcelain crucible.

Evaporate to dryness in the crucible, ignite gently to expel ammonia salts, and finally over the full flame of a good Bunsen or Teclu burner. Cool and weigh as WO_3.

If the ore is of low grade, the evaporation should be made in a platinum dish, and the residue, after ignition, moistened with hydrofluoric acid and again ignited before weighing as WO_3.

11. **Fusion Method for Wolframite.**—Fuse 0.5 gram of the very finely ground ore with 2–3 grams of sodium potassium carbonate in a platinum crucible for from one-half to three-quarters of an hour. Dissolve the fused mass in boiling water. The tungsten goes into solution as sodium or potassium tungstate, together with alkali silicate and also stannate, if tin be present. The residue contains the iron, manganese, calcium, and magnesium. Filter and wash with hot water. Rinse the residue into a beaker and warm with dilute hydrochloric acid. If gritty particles remain undissolved, filter them off through the filter last used and wash with hot water. Dry and ignite the residue and again fuse it with the mixed carbonates. Dissolve the fused mass as before, filter and unite the filtrate with the first filtrate.

12. Having thus obtained an aqueous solution of alkali tungstate, add to it an excess of nitric acid and evaporate to dryness on a water-bath. Again add a little nitric acid and evaporate to dryness a second and a third time. Finally heat the residue in a drying-oven at 120° C. for some time, then moisten with strong nitric acid and allow to stand for fifteen or twenty minutes. Now add a hot 5 per cent solution of ammonium nitrate and filter the mixture, washing well with ammonium nitrate solution slightly acidified with nitric acid to remove all the sodium and potassium salts. Finally, wash once or twice more with a hot, very dilute ammonium nitrate solution and then dry the

filter and contents and transfer the latter as completely as possible to a weighed platinum crucible. Moisten the paper with a strong solution of ammonium nitrate, dry it and incinerate over the crucible in a coil of platinum wire. Ignite the whole, now, with free access of air. If the tungstic acid is not pure yellow when cool, moisten with a few drops of nitric acid and repeat the ignition.

13. The ignited tungstic acid may contain silica and stannic oxide. The former may be removed by warming with a few cubic centimeters of hydrofluoric acid, evaporating to dryness and igniting. The residue consists of pure tungstic acid, or tungstic acid and stannic oxide. The amount of the latter is usually so small as to be negligible. If desired, however, the tin may be volatilized as stannic chloride by ignition with ammonium chloride. The stannic chloride is decomposed by the moisture of the air and stannic oxide may be deposited on the outside of the crucible. To prevent this, place the crucible in a larger one and keep the outer crucible covered until the ammonium chloride is completely expelled. Now heat the inner crucible with free access of air until its contents become pure yellow. Cool and weigh. Repeat the ignition with six or eight times as much ammonium chloride as there is precipitate until the weight of the residual WO_3 becomes constant. The tungstic acid becomes dark on igniting in the absence of air and assumes its true color and weight only on igniting with free access of air.

The weight of the WO_3 multiplied by 0.793 gives that of the tungsten.

14. Another method of precipitating the tungstic acid from the solution of alkali tungstate is that of Berzelius, as follows: Neutralize the greater part of the alkali with nitric acid, being very careful, however, to still leave the solution slightly alkaline. The amount of nitric acid to use is best ascertained by a blank test on the same amount of alkali carbonates as was taken for the fusion. Now add a solution of mercurous nitrate until it produces no further precipitation. If, on slowly adding the mercurous nitrate, the precipitate seems to be getting unduly large, indicating too great alkalinity, add nitric acid drop by drop until an added drop of mercurous nitrate produces no cloud. Heat to boiling, allow the precipitate to settle, then filter and wash with water containing mercurous nitrate. Dry the filter and contents and then ignite in a platinum crucible under a hood. Weigh as WO_3.

The tungstic acid thus obtained almost always contains silica and possibly stannic oxide. It may be purified as described above (13).

15. The Determination of Tungstic Acid in Low-grade Ores.*— Weigh 5 grams or more of the sample. Digest in a 4-inch porcelain dish with 20 cc. of a 25 per cent solution of sodium hydroxide (free from chloride) for thirty to forty-five minutes on a water-bath. Now dilute the mixture somewhat, add a little sodium peroxide to oxidize any decomposition products of sulphides, transfer to a 250-cc. measuring-flask and make up to the mark. After mixing, filter through a dry filter, reject a little of the first filtrate that runs through, and collect 200 cc. of the remainder in a measuring-flask. Transfer this portion to a beaker, acidify with nitric acid and then make alkaline with ammonia. Heat to boiling, filter and wash. Acidify the filtrate slightly with dilute nitric acid, add mercurous nitrate solution (prepared as below) in excess, and then a few drops of dilute ammonia On warming and stirring, the precipitate settles readily. Filter, wash the precipitate with weak mercurous nitrate solution, and then ignite the precipitate and paper together in a weighed porcelain crucible. A platinum crucible may be used if the ore is free from arsenic. Weigh as WO_3.

For assays of ores and tailings, the sample may be reduced to a sufficient degree of fineness in a wedgwood mortar, but for concentrates an agate mortar is necessary; fine powdering is essential. For decomposing charges containing not more than 0.4 gram of tungstic acid, 20 cc. of a 25 per cent solution of sodium hydroxide will suffice. The decomposition is rapid; 0.4 gram of wolfram concentrates being decomposed in fifteen minutes to the extent of 98 per cent of the tungsten content. As a rule, however, it is best to take from thirty to forty-five minutes for the decomposition.

The mercurous nitrate solution may be conveniently prepared from mercury. Digest from 2 to 3 ozs. in a large beaker or flask for $1\frac{1}{2}$ hours with 25 cc. of nitric acid (sp. gr. 1.4) and 75 cc. of water, on a hot plate which will keep the liquid nearly at the boiling-point. Allow to stand, hot, overnight. Dilute to about 400 cc., which will give a saturated solution with a minimum of free acid.

The weighed WO_3 may be tested for silica, if desired, by treatment in platinum with hydrofluoric acid. The loss is usually very slight.

In the presence of scheelite the method is not applicable, since this mineral is only partially attacked, under the conditions of the assay.

* H. W. Hutchin and F. J. Tonks, Inst. Min. and Met. Bull., No. 56.

CHAPTER XXIX

URANIUM AND VANADIUM

METHOD 1 is a modification of Method 2. It is considerably shorter than the latter and apparently quite as accurate.

1. Gravimetric Method for Uranium in Ores.—Take 0.5 gram of the finely ground ore, or more, according to richness. Treat by heating gently in an 8-oz. " copper flask " with nitric or hydrochloric acid, or both, as the nature of the ore appears to require. Unless there is much galena or iron oxide, use nitric acid, taking 10 cc. and adding also about 2 cc. of hydrofluoric acid. With much galena or iron oxide it is best to start with 10 cc. or more of hydrochloric acid to get these constituents into solution. Whenever hydrochloric acid is used, boil almost to dryness to expel most of it before continuing. To this residue add the nitric and hydrofluoric acids as above. In any case, boil very gently to effect complete decomposition and then, finally, to approximate dryness. Allow to cool, add 3 cc. of nitric acid and 50 cc. of hot water, and heat to dissolve everything soluble.

Now make slightly alkaline with ammonia, then just acid with nitric acid, and again alkaline with a little solid ammonium carbonate, followed by about 5 cc. of strong ammonia and 3–4 grams more of ammonium carbonate.[1]

Boil for about a minute and then filter, having a wetted wad of absorbent cotton in the apex of the filter. Wash twice with hot water. Boil and concentrate the filtrate in a covered beaker during the next step.

Dissolve the precipitate on the filter with a little hot dilute nitric acid, receiving the filtrate in the original flask. Again neutralize and precipitate as before, washing this second precipitate well with hot water. Add the filtrate to the first one and continue the concentration to 150–200 cc. Now acidify with nitric acid, and then, in case of doubt, add about 1 cc. of hydrogen peroxide. A reddish-brown color indicates vanadium.

A. *Vanadium Present.*—Boil to expel any remaining CO_2, make just alkaline with ammonia, then just acid with nitric acid, finally adding about 4 cc. of the latter in excess. The appearance of the liquid is usually a sufficient indication of the neutralization points. Now add 1 gram of lead acetate crystals and then sufficient ammonium acetate solution (about 20 cc.) to neutralize the nitric acid and precipitate the lead vanadate. Boil for about ten minutes, allow to settle somewhat and then filter through a double filter into a large beaker, returning the first portions if not perfectly clear. Wash well with hot water.[2] If the filtrate is bulky, boil down to perhaps 200–250 cc. Now add ammonia in marked excess and boil for about a minute to expel any CO_2. Filter hot, paying no attention to a turbid filtrate unless it is yellowish. (In such a case, wash the precipitate once with hot water, then acidify the filtrate with nitric acid and again precipitate with ammonia as before and pour through the first precipitate.) No washing required.[3]

Place the last beaker under the funnel and fill the latter with a strong hot solution of ammonium carbonate to which some free ammonia has been added. Usually one filling is sufficient to dissolve all the uranium and leave a white residue of lead carbonate, perhaps slightly discolored by a trace of iron.[4] Wash with hot water, using a little more of the ammonium carbonate solution, if apparently necessary. Add to the filtrate sufficient strong hydrogen sulphide water (ordinarily, 25 cc.) to precipitate all the remaining lead, or pass the gas for a short time. This also removes traces of iron. Heat to boiling, then allow to stand and settle. Filter, washing with hydrogen sulphide water containing a little ammonium carbonate. Boil to expel the hydrogen sulphide, then acidify with nitric acid and boil off all CO_2. Continue according to C.

B. *Vanadium Absent.*—Boil the nitric acid solution sufficiently to expel all CO_2, then add ammonia in marked excess and boil a little longer to expel any CO_2 in the ammonia. Filter the hot mixture, returning the first portions if not perfectly clear. No washing required. Dissolve the uranium on the filter with hot ammonium carbonate solution, as described in the last paragraph, and continue from this point as in the same situation above. Do not omit the hydrogen sulphide treatment, for, even in the absence of lead, there will usually be traces of iron to remove. Continue according to C.

C. Add ammonia in marked excess, boil well for about a minute and then filter through an ashless filter, returning the first portions if not clear. No washing required. Ignite filter and precipitate thoroughly in a porcelain crucible and weigh, after cooling, as U_3O_8. Impurities are usually present.

Dissolve the residue in the crucible by warming with a little nitric acid. Dilute a little and test for vanadium with hydrogen peroxide. A slight brownish tinge may be neglected. Rinse the solution into a small beaker, add solid ammonium carbonate in excess, boil a minute or two and then filter through a small filter, washing with hot water. The residue on the filter may consist of alumina, iron oxide and other insoluble matter. Ignite filter and residue in the original crucible, weigh and deduct the weight from that of the impure U_3O_8 previously found

Ammonium Acetate Solution.—Eighty cubic centimeters of strong ammonia, 100 cc. of water and 70 cc. of 99 per cent glacial acetic acid.

Note.—A yellow filtrate from the ammonium uranate indicates incomplete precipitation. This may be due to a deficiency in ammonium nitrate, as ammonium uranate is perceptibly soluble in pure water. Acidify the filtrate with nitric acid and re-precipitate with ammonia, filtering through the main precipitate; or, better, dissolve the precipitate on the filter with hot dilute nitric acid, so that the mixed filtrates will be markedly acid, and repeat the precipitation with ammonia. The filtrate should be colorless.

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[1] The idea is to get the solution just faintly acid and then make alkaline with ammonium carbonate instead of ammonia. Ammonia would cause a precipitation of ammonium uranate at the same time that the ferric hydroxide came down. This would result in a large occlusion of ammonium uranate and a very incomplete re-solution by the ammonium carbonate subsequently added. If the final alkalinity is produced by ammonium carbonate instead of ammonia, the occlusion of the uranium is much less, and a repetition of the precipitation frees practically all the remaining uranium.

[2] The vanadium should now be all removed and on the filter; but the precipitated lead vanadate is very fine and a little is liable to run through at the outset. Be sure that the filtrate is perfectly clear.

[3] The uranium is now on the filter as ammonium uranate. It may be mixed with more or less ferric and lead hydroxides, silica and alumina. These impurities could not all be washed out, and, as they will be mostly removed subsequently, washing is superfluous. A white turbid filtrate would be simply due to lead in the form of hydroxide or carbonate (getting CO_2 from the air on exposure).

[4] Most of the lead hydroxide that remained with the ammonium uranate remains on the filter as carbonate, while a little lead and all the uranium goes into the filtrate. This small amount of lead is easily removed by H_2S.

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2. Gravimetric Method 2 for Uranium in Ores.—Treat 1 gram of the ore (or more if very low grade) in an 8-oz. flask with 10 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid. Allow to simmer gently over a low heat until solution is as complete as possible, and then boil to dryness. This may be done by manipulating the flask in a holder over a free flame. Add 3 cc. of hydrochloric acid and 5 cc. of water to the residue, warm for a short time, occasionally agitating, then dilute with 25 cc. of hot water and filter, washing with warm water. Receive the filtrate in a small beaker.

3. Pass hydrogen sulphide into the liquid to separate copper, lead and other metals of this group, filter, wash with hydrogen sulphide water, and boil the filtrate to expel the hydrogen sulphide. Concentrate to 100 cc. if necessary, oxidize with hydrogen peroxide (usually 10 cc.), and then neutralize with dry sodium carbonate, adding 2 or 3 grams in excess. Boil the liquid for about fifteen minutes, or until the yellowish uranium precipitate dissolves, leaving a brown precipitate which is largely iron. Filter and wash the iron precipitate once or twice with hot water, and reserve the filtrate. Dissolve the iron precipitate in the least possible amount of nitric acid (1 : 1), dilute somewhat if necessary, add 10 cc. of hydrogen peroxide and repeat the precipitation with sodium carbonate precisely as before. Filter into the beaker containing the first filtrate. Wash well with hot water.

4. Evaporate the united filtrates from the iron precipitation to a volume of about 200 cc., add 10 cc. of strong nitric acid and boil until all CO_2 is expelled. Neutralize the free acid with ammonia (until a slight permanent precipitate appears), then add 4 cc. of nitric acid for each 100 cc. of liquid. Now add 10 cc. of a 20 per cent lead acetate solution, and enough of a strong solution of ammonium acetate to neutralize the nitric acid present and substitute acetic acid for it. The object is to precipitate the vanadium as lead vanadate in an acetic acid solution. The ammonium acetate solution may be made by mixing 80 cc. of strong ammonia, 100 cc. of water, and 70 cc. of acetic acid 99 per cent pure.

5. Heat the liquid containing the lead vanadate precipitate on

the steam-bath for one hour or more, filter on a close filter and wash with warm water. Dissolve the precipitate in the least possible quantity of hot dilute nitric acid, neutralize as before, add 3 cc. of nitric acid in excess, then 2 cc. of lead acetate solution and repeat the precipitation of lead vanadate by adding ammonium acetate in excess. Filter and add the filtrate to the one from the first precipitation of lead vanadate. Evaporate the united filtrates from the lead vanadate to about 400 cc. Add 10 cc. of strong sulphuric acid to separate the bulk of the lead (derived from the excess of lead acetate) as $PbSO_4$, and filter, washing the precipitate with cold water. Neutralize the filtrate from the $PbSO_4$ with ammonia and add freshly prepared $(NH_4)HS$ until the solution is yellow and the uranium and what little lead is present are precipitated as sulphides. Warm the mixture gently until the sulphides settle well. Filter and wash slightly with warm water.

6. Dissolve the precipitate in a No. 2 beaker with hot dilute (1 : 2) nitric acid, add 5 cc. of strong sulphuric acid and evaporate until the latter is fuming. Cool, take up with water, boil, let the small precipitate of $PbSO_4$ settle until the liquid is cold, and then filter it off, washing with very dilute sulphuric acid (1 : 20).

7. *Separation of Alumina.*—Nearly neutralize the filtrate with ammonia. Have the solution cold (not warmer than 30° C.), and add powdered ammonium carbonate in about 2 grams excess. This will precipitate the aluminum and hold the uranium in solution. Let the precipitate settle, filter, and wash it with warm water. If the precipitate is bulky, or is at all yellow, dissolve it in a little dilute sulphuric acid and reprecipitate with ammonium carbonate as before.

8. Acidify the filtrate, or combined filtrates, from the alumina with sulphuric acid and boil to thoroughly expel CO_2. Make the liquid slightly alkaline with ammonia while it is hot, and heat gently until the ammonium uranate collects and settles. Filter and wash with a very dilute solution (2 per cent) of ammonium nitrate. Do not allow the precipitate to run dry on the filter after the first washing. Dry the precipitate, ignite it in a porcelain crucible and weigh as U_3O_8. Dissolve the ignited residue in a little nitric acid and test it with H_2O_2 for vanadium. Only a faint brownish tint should appear, at most. Rinse the solution into a small beaker and test for alumina with ammonium carbonate. Should an appreciable amount be found it may be filtered off, ignited, weighed and deducted.

9. Volumetric Method for Uranium.—Treat 1 gram of the ore (or more if very low grade) in an 8-oz. flask with 10 cc. of strong hydrochloric acid and 5 cc. of strong nitric acid. Allow to simmer gently over a low heat until solution is as complete as possible, and then boil to dryness. This may be done by manipulating the flask in a holder over a free flame. Add 3 cc. of hydrochloric acid and 5 cc. of water to the residue and warm gently until solution is as complete as before. Now add 35 cc. water and pass in hydrogen sulphide to precipitate the members of that group. Filter, washing with hydrogen sulphide water at least seven times, receiving the filtrate in a fairly large beaker. Placing a boiling-rod (p. 8) in the liquid, cover the beaker and boil off the hydrogen sulphide. Remove from the heat and add 10 cc. of H_2O_2. Now add dry sodium carbonate in small portions until the free acid is neutralized and then about 2 grams in excess. Boil the mixture until all CO_2 is expelled and the precipitate, on standing, settles well. At this point add about 2 cc. more H_2O_2. Filter, washing once or twice with hot water, and reserve the filtrate, which may be allowed to boil and concentrate while waiting for the next step. Rinse the bulk of the precipitate from the filter back into the beaker, then place the latter under the funnel and dissolve what precipitate remains on the filter with dilute (1 : 1) nitric acid, using as little as possible. Now wash the filter well with hot water, allowing all to run into the beaker containing the precipitate. Warm the mixture until the precipitate dissolves, adding more acid if necessary, then add H_2O_2 and precipitate with sodium carbonate precisely as before. Filter and wash the precipitate well with hot water. Add the filtrate to the first one, which has been concentrating, and boil the whole to a bulk of about 100 cc. Now remove from the heat (simply to prevent frothing over) and cautiously add 10 cc. of strong nitric acid, and then boil again until all the CO_2 is expelled. The solution must be clear and boiling hot for the next step.

10. *Separation of Vanadium.*—Place in a large beaker about 15 grams of ammonium acetate, 5 grams of microcosmic salt, 50 to 75 cc. of water, 5 cc. of glacial acetic acid. Place a boiling-rod in the mixture and heat to rapid boiling. Have arranged over the beaker a funnel with the lower end drawn out so as to deliver only a fine stream. Pour the hot uranium solution through this into the boiling phosphate solution. Allow to boil a few minutes after all has run through. Now remove the beaker from the heat, cover it and allow to stand until

the precipitate has settled well and then filter. Time will be saved by pouring as much as possible of the clear liquid through the filter before disturbing the precipitate. Wash the precipitate only once, using hot water. Now rinse it back into the beaker, place the latter under the funnel and dissolve what remains on the filter with a little hot, dilute nitric acid. Six cubic centimeters of 1 : 1 acid are usually sufficient. Wash the filter well with hot water, receiving all in the beaker containing the precipitate. Warm the mixture until the precipitate dissolves and dilute to about 75 cc., if necessary. Heat to boiling and repeat the phosphate precipitation precisely as before. The two operations will remove practically all the vanadium and leave the uranium and aluminum as phosphates. Filter as before and wash four or five times with hot water containing a little ammonium sulphate. This is tedious if there is much aluminum present. Time is saved by stirring the precipitate in the apex of the filter with the jet each time. Use the same filter as before.

11. Make a mixture, in a small beaker, of 5 cc. of strong sulphuric acid and 15 cc. of water, and heat nearly to boiling. Place an 8-oz. flask under the funnel and pour the hot acid mixture slowly over the precipitate on the filter. With care, it may thus be all dissolved, although the hot acid may be poured through again if necessary. Wash the filter well with hot water, but do not unduly increase the volume of liquid in the flask. This should not be allowed to much exceed 50 to 75 cc. Heat nearly to boiling and run in permanganate to a permanent deep pink color, to oxidize any organic matter present. Now add 10 grams of 20-mesh C. P. zinc and allow to stand until the action has become very slow, then add 25 cc. more water and 10 cc. more sulphuric acid. When the zinc has nearly all dissolved, filter the solution through a fresh filter, washing the latter and residue well with cold water. Receive the filtrate in a 16-oz. flask. Dilute with cold water, if necessary, until the flask is about half full.

12. Cool the solution to room temperature and titrate with the ordinary permanganate solution used for iron (p. 104) until a single drop produces a pink color that lasts several seconds. The end-point is very sharp, although the color may soon fade, owing, possibly to traces of vanadium. Note the burette-reading and deduct the correction required for the iron in the 10 grams of zinc used, this having been determined by a blank test. As a rule, no further correction is required, as any trace of vanadium present appears to be

acted on so slowly in the cold as not to seriously interfere with obtaining a sharp end-point. As a precaution, however, add 1 gram of sodium sulphite and boil the solution in the flask until all smell of SO_2 has gone, and then seven or eight minutes more. Add cold water to restore the original volume, cool to room temperature and titrate as before. Run the above zinc blank in the same way and find the correction required for the combined iron and impurities in the sulphite. After deducting this from the last reading, the remainder, if any, may be credited to vanadium and deducted as a further correction from the uranium reading.

13. 55.84 Fe = 140.43 U_3O_8, or 1 Fe = 2.515 U_3O_8. If the percentage value of 1 cc. of the permanganate for iron, based on 0.5 gram of ore taken, is given, this, multiplied by 1.257, will give the percentage value of 1 cc. for U_3O_8, when 1 gram of uranium ore is taken.

14. **Method for Vanadium.*** Treat 1 gram of the finely divided ore in a platinum dish with about 3 cc. of strong sulphuric acid and 20 cc. of hydrofluoric acid. Evaporate to fumes of sulphuric acid and then expel the latter by heating over a naked flame. Now add about 2 grams of sodium carbonate, and fuse. Extract the melt with hot water and filter, washing with hot water. Acidify the filtrate with sulphuric acid, heat nearly to boiling and pass in hydrogen sulphide gas to saturation. Arsenic and molybdenum are precipitated, if present, and V_2O_5 is reduced to V_2O_4. Filter, washing with hydrogen sulphide water. Boil the filtrate until the hydrogen sulphide is completely expelled and then titrate the hot solution with a standard solution of potassium permanganate to the usual pink tinge (IRON, 8). Then again reduce by passing in sulphur dioxide gas, boil off the excess and repeat the titration. The latter result is apt to be a little lower than the former, and is to be taken as the correct one. The iron factor of the permanganate multiplied by 0.9135 will give the vanadium factor;[1] care must be taken to use the absolute iron factor and not the percentage factor based on 0.5 gram of ore being taken for analysis. Uranium does not interfere with this method, which is an excellent one where a single determination has to be made.

15. The direct use of a solution of sulphur dioxide, or an alkali sulphite for reducing the vanadium is inadmissible unless these have been freshly prepared, or a blank is run, since they are liable to con-

* Adapted from Hillebrand and Ransome, Am. Jour. Sci., x, also Hillebrand, Bulletin 176, U. S. Geological Survey.

tain other oxidizable substances than SO_2 or a sulphite. The SO_2 is best obtained as wanted by heating a flask containing a solution of SO_2, or a sulphite to which sulphuric acid has been added.

16. In case the volume of permanganate used is so small as to make the presence of vanadium doubtful, it is necessary to apply a qualitative test, which is best made as follows: The solution is evaporated and heated to expel the excess of sulphuric acid, the residue is taken up with 2 or 3 cc. of water and a few drops of dilute nitric acid and a couple of drops of H_2O_2 are added. A characteristic brownish tint indicates vanadium. Unless the greater part of the free sulphuric acid has been removed the appearance of the color is sometimes not immediate and pronounced, hence the necessity for the above precaution. It is also necessary that the nitric acid shall be in considerable excess, since in neutral or only faintly acid solution the color does not appear strongly.

For determining very small amounts of vanadium in rock analysis the titrated liquid should be from 25 to 100 cc. in bulk and the permanganate solution very dilute, 1 cc. = about 0.001 gram V_2O_5. The temperature for titration should be from 70°–80° C.

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[1] When ferrous iron is oxidized to ferric, the change may be expressed as follows: $2FeO+O=Fe_2O_3$. Thus, every $2Fe=O$. In the case of vanadium, $V_2O_4+O=V_2O_5$. V_2, then, $=O$. This makes $Fe_2=V_2$, or, $Fe=V$. The relations by weight are in accordance with the atomic weights; 55.84 Fe = 51 V, or, 1 Fe = 0.9135 V.

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17. Volumetric Method for Carnotite.*—This mineral contains uranium and vanadium as potassium uranyl vanadate.

Dissolve a sample of the ore that does not contain more than 0.25 gram of U_3O_8 in sulphuric acid (1 : 5) and evaporate to fumes of the acid. Cool, dilute, add an excess of sodium carbonate and boil until the precipitate settles well. Filter and wash with hot water. Dissolve the precipitate in the smallest possible amount of sulphuric acid (1 : 5), dilute, add an excess of sodium carbonate, boil, filter and wash. Acidify the combined filtrates and wash-waters with sulphuric acid. Add ammonium phosphate (0.5 gram is usually sufficient), heat to boiling and make alkaline with ammonia; boil for a few minutes, filter and wash with hot water containing a

* A. N. Finn, Jour. Am. Chem. Soc., XXVIII, 1443.

little ammonium sulphate, which prevents the finely divided particles of the precipitate from passing through the filter.

18. The filtrate now contains the vanadium, and the precipitate the uranium. Acidify the filtrate with sulphuric acid, pass sulphur dioxide into it until it becomes blue, boil to expel the excess of sulphur dioxide and titrate while hot with standard potassium solution. The iron factor of the permanganate multiplied by 1.63 will give the V_2O_5 factor, or, by 0.9135, the V factor.[1]

19. Dissolve the ammonium uranyl phosphate in dilute sulphuric acid, add some granulated zinc and let the action continue vigorously for at least thirty minutes. Remove the undissolved zinc by filtering through asbestos, using a suction pump. (These are Finn's directions; I would suggest a plug of absorbent cotton placed in the neck of a loop funnel, which will give sufficient suction, instead of the asbestos and suction pump.) Titrate the filtrate at about 60° C. with permanganate (twentieth-normal).*

The iron factor of the permanganate solution multiplied by 2.516 will give the U_3O_8 factor, or, by 2.133 the U factor.[2]

Note.—The above method is given practically according to Finn's description. I would suggest that a source of error lies in the separation of the vanadium, which I have never found to be complete with a single precipitation of uranium as phosphate. It would be well, also, to run blanks with the permanganate and make the necessary deductions.

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[1] See note following **16** regarding the factor 0.9135. $V_2 : V_2O_5 = 0.9135 : x$, or, $102 : 182 = 0.9135 : x$. $x = 1.63$.

[2] $UO_2 + O = UO_3$; this gives $U = O$. $2FeO + O = Fe_2O_3$; this gives $2Fe = O$, and $2Fe = U$, or 111.68 Fe = 238.2 U. This gives 1 Fe = 2.133 U. Similarly, $3Fe_2 = U_3O_8$, or, 332.04 Fe = 842.6 U_3O_8. This gives 1 Fe = 2.516 U_3O_8.

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20. Method for Vanadium in Ores.†

Special solutions required:

A very dilute solution of potassium ferricyanide; about 50 mg. dissolved in 100 cc. of water.

A 20 per cent solution of ferrous sulphate or ferrous ammonium sulphate.

* I would advise making a blank test and deducting the permanganate required.

† This is the method I ordinarily employ.

Procedure.—Weigh 0.5 gram (or 1 gram if of very low grade) of the finely ground ore into an 8-oz. flask. Add 5 grams of anhydrous sodium sulphate, 5–6 cc. of strong sulphuric acid and about as much hydrofluoric acid as can be held in an ordinary platinum crucible cover. (The hydrofluoric acid is advisable, although not always necessary.) Heat over a strong free flame, with the flask in a holder, nearly to a melt. Allow to cool while distributing the mass around the sides of the flask. This prevents the solidifying cake from cracking the flask and also facilitates subsequent solution. It is best, but not necessary, to use a Pyrex flask.

The above treatment will usually effect complete decomposition; but if it fails, try the addition of one-eighth of a 9-cm. filter paper at the outset. The organic matter must, of course, be entirely burned off.

21. When the flask is sufficiently cool, add 50 cc. of cold water and 10 cc. of strong sulphuric acid, and boil to dissolve everything soluble. Now, add 5 cc. of syrupy phosphoric acid, and then, from a burette, run potassium permanganate solution into the hot liquid until a decided red color is obtained that persists after boiling again. Use the same permanganage as will be employed in the subsequent titration.

Transfer the hot solution from the flask to a 400-cc. beaker and dilute to about 200 cc. with hot water.

22. Have ready a spot plate and place a drop of the ferricyanide solution in each of the depressions.

Using a small pipette, add the ferrous solution in small portions at a time, very cautiously, finally drop by drop, to the hot liquid in the beaker, testing after each addition, until a drop of the vanadium solution, taken up on a glass rod and allowed to fall on a ferricyanide test, produces a blue color.

The ferrous solution first decolorizes the permanganate, then reduces the V_2O_5 to V_2O_4, and when finally in slight excess, it shows a blue color with the ferricyanide. Try to avoid an unnecessary excess of the ferrous solution. The excess of ferrous salt must now be oxidized to ferric. Run the regular permanganate solution in from the burette until the ferricyanide test fails to develop a blue tinge after standing about half a minute. This should be done as carefully as in a regular titration, as faint tinges of color develop slowly and should be waited for. Toward the last the permanganate should be added a drop at a time.

the permanganate, even though the test soon becomes blue. The point is a delicate one but not difficult to attain, and is very important.[1]

23. Titrate the still hot liquid with standard potassium permanganate solution until a very faint pink tinge is obtained that persists for at least a minute, when it may change to brownish.

With a permanganate solution containing 1.737 grams per liter, 1 cc. = 1 per cent V_2O_5 on the half-gram basis.[2] This is a convenient strength for ordinary cases. Standardize it against about 0.125 gram of sodium oxalate (Sorensen's salt). The percentage value of 1 cc. in sodium oxalate multiplied by 0.7612 will give the percentage value in V, or, multiplied by 1.358 will give the percentage value in V_2O_5. (0.125 gram = 25 per cent on the half-gram basis.)[3] The permanganate ordinarily used for iron is rather strong for accurate work; its Fe value multiplied by 1.63 will give the V_2O_5 value.[4] The percentage of V_2O_5 is ordinarily required.

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[1] The reducing action of a ferrous solution on V_2O_5 appears to be sufficiently reversible to cause a blue tinge to show, in a short time, in a test that was at first colorless. The V_2O_4 that has been formed becomes slightly oxidized again to V_2O_5, reducing a corresponding amount of the ferric salt to ferrous. This occurs in a test that was at first just colorless, soon causing it to show a blue tinge. This slight reversing action which is simultaneously occurring in the main solution has no effect on the titration, the oxidation of the V_2O_4 being just balanced by the ferrous iron produced.

[2] 2 $KMnO_4$, or, $K_2O.Mn_2O_7$, has 5 oxygen atoms available for oxidation in this reaction, the Mn_2O_7 being reduced to Mn_2O_2. 2 $KMnO_4$, then, may be considered to $=O_5$. The oxidation of the vanadium is in accordance with $V_2O_4+O=V_2O_5$. This gives $V_2O_5=O$. Then, 2 $KMnO_4=O_5=5$ V_2O_5, or 316.06 parts by weight of $KMnO_4=910$ parts of V_2O_5. One per cent of 0.5 gram is 0.005 gram. The amount of $KMnO_4$ corresponding to this weight of V_2O_5 is found by the proportion $316.06 : 910 = x : 0.005$. $x=0.001737$. This is the amount of $KMnO_4$, in grams required to be in 1 cc. to equal 1 per cent of V_2O_5. This gives 1.737 grams per liter.

[3] One molecule of sodium oxalate, $C_2O_4Na_2$, requires 1 atom of oxygen for its oxidation in the titration. V_2O_4 also requires 1 oxygen atom; consequently, $C_2O_4Na_2=V_2O_4$ or V_2O_5 or V_2. That is, 134.01 parts by weight of sodium oxalate = 182 parts by V_2O_5 or 102 parts of V. This gives 1 part of sodium oxalate = 1.358 parts of V_2O_5 or 0.7612 part of V.

[4] $2FeO+O=Fe_2O_3$, therefore, $2Fe=O$. $V_2O_4+O=V_2O_5$, therefore $V_2O_4=O=V_2O_5$. This gives $2Fe=V_2O_5$, or, 111.68 parts by weight of Fe = 182 parts of V_2O_5, that is, 1 part of Fe = 1.63 parts of V_2O_5.

24. Vanadium by Hydrochloric Acid Method of Reduction.*—Weigh 1–5 grams of the finely ground ore into a 16-oz. flask. Add 30 cc. of 1 : 1 sulphuric acid and boil to fumes. The insoluble gangue is liable to make the mixture bump badly. Use a boiling rod, agitate the flask frequently, and, if necessary, run down by hand. Maintain at fuming point for ten minutes. Allow to cool and then dilute to about 75 cc. If the bumping was bad, filter at this point and then return liquid to flask. Heat somewhat, and add sufficient powdered potassium permanganate to produce a strong pink color that persists on boiling. This destroys any organic matter.

25. Cool slightly and add 50 cc. of strong hydrochloric acid. Boil gently, nearly to fumes. About 15 cc. of strong sulphuric acid should still be present to keep all salts in solution. Again cool sufficiently and add 25 cc. more of hydrochloric acid. Boil nearly to fumes once more and note the color, which, in the absence of much iron, should be pure blue. If greenish (unless much iron is present), repeat the boiling with more hydrochloric acid until blue. Organic matter, unless previously destroyed, would make trouble here.

26. Finally, continue the boiling to strong fumes. Fume about a minute and then allow to cool completely. Dilute to about 200 cc. with cold water, heat nearly to boiling and titrate to the usual pink tinge with standard potassium permanganate solution.

The calculation is the same as described in **23**; note, however, that the percentage factor for iron, with permanganate standardized on the 0.5 gram basis, should not be used, unless in this case 0.5 gram was also taken for analysis. Calculate from the absolute factor for iron.

Note.—The crux of this method is, of course, the reduction of V_2O_5 to V_2O_4 by boiling with hydrochloric acid. This appears to depend upon the reaction

$$V_2O_5 + 2HCl \rightleftarrows V_2O_4 + H_2O + 2Cl.$$

The free chlorine naturally makes the reaction easily reversible. Some of the chlorine reacts to oxidize the V_2O_4 again and some is lost by volatilization. Owing to this loss of chlorine, the amount of reduction gradually increases by the continued action of more hydrochloric acid until it is practically complete. This is why so much hydrochloric acid and such long boiling are required.

* Ledoux & Co.

CHAPTER XXX

ZINC

1. The following method, developed by the writer, for the technical estimation of zinc in ores, etc., is of general but not of universal application. Ordinarily, however, almost the only source of trouble likely to be encountered is the preliminary decomposition of the ore. The method as described is applicable to the usual run of mixed sulphide ores and many oxidized ores. When the decomposition fails or is doubtful, the operator must note the fact and apply the proper remedy. Some observations on this and related matters are given below.

2. Author's Method.—Prepare a solution of potassium ferrocyanide containing 21.54 grams of the crystallized salt to the liter.[1] Standardize this solution as follows: Weigh carefully about 0.2 gram of pure zinc into an 8-oz. flask and add 10 cc. of strong hydrochloric acid (sp. gr. 1.20). When the zinc has dissolved, dilute with about 25 cc. of water, add a few drops of litmus solution as an indicator, and make slightly alkaline with ammonia. Again acidify slightly with hydrochloric acid and then add 3 cc. of the strong acid in excess. Dilute now to about 300 cc. with hot water and heat nearly to boiling. Titrate with the ferrocyanide solution as follows: Pour about two-thirds of the zinc solution from the flask into a 400-cc. beaker. Run the ferrocyanide solution from the burette into this portion, a few cubic centimeters at a time, until a drop, when removed and tested on a porcelain plate with a drop of a 15 per cent solution of uranium nitrate, shows a brown tinge. Now add more of the zinc solution from the flask and continue the titration more cautiously until the end-point is again passed. Proceed thus, adding more of the reserved portion in such amounts as may appear advisable, passing the end-point each time with greater caution. Finally, add the last of the reserved portion, and then, to save rinsing out the flask, pour a large part of the solution back into it again and then empty it once more into the

beaker. From this point finish the titration very carefully, ordinarily by testing after each addition of two drops. The reaction is sharper if, instead of a single drop of the zinc solution, a quantity equivalent to several drops be taken for the test. If this is done only near the end of the titration the amount of zinc lost thereby will be insignificant. A convenient way of making the test is to use a small pipette and place one or two drops of the uranium solution in each depression of the test-plate at the outset. By using a glass tube instead of a rod for a stirrer, any desired quantity of the solution can be quickly removed for a test. When the final brown tinge is obtained, note the reading of the burette, and then wait a minute or two and observe if one or more of the preceding tests do not also develop a color. The end-point is always passed by a test or two and the burette reading must be corrected accordingly. Deduct for as many tests as show a color and for 1 drop additional, since 2 drops are required to show a test when no zinc is present. One cubic centimeter of the standard solution will equal about 0.005 gram of zinc, or in the case of ores, about 1 per cent. when 0.5 gram is taken for assay.

3. **Regular Method for Ores.**—A modification of the method of decomposition described below is sometimes necessary. Some ores require a more or less prolonged treatment with hydrochloric acid, to insure complete decomposition of oxides, before adding nitric acid. Ores that gelatinize should be mixed with a little water before any acid is added, and then the acid should be added while the flask is being agitated, to prevent setting or caking. This is to be followed by occasional agitation during decomposition. Other cases will be referred to later.

Weigh 0.5 gram of the ore into a 500-cc. Erlenmeyer flask. Add 5 cc. of strong hydrochloric acid and 10 cc. of strong nitric acid. It is highly advantageous, in many cases, to also add about 2 cc. of hydrofluoric acid—as much as can be held in the hollow of an ordinary platinum crucible cover. This tends to prevent any possible trouble from gelatinous silica. One must be certain, however, when this acid is used, that the material of the flask contains no zinc. On this account I advise the use of Pyrex flasks, which are free from zinc.

Boil gently until only a few cubic centimeters of liquid remain, but endeavor not to take to dryness. Remove from the heat and add 15 cc. of strong nitric acid and 5 grams (usually measured, after trial,

in a small crucible) of potassium chlorate. (Mallinckrodt's " Pure Granular " is convenient for measuring.)

Replace the flask over a gentle heat and run just to dryness. If the mixture shows a tendency to " bump," use a small watch-glass cover, raised slightly on one side with a bit of bent glass tubing, to allow escape of vapors, removing it again when the danger has passed. Hard dryness is unnecessary except when gelatinous silica is present, and even in this case there should be no overheating or fusing of the salts. With other ores it is sufficient to run just to dryness and remove at once from the heat.

It is ordinarily more satisfactory, toward the end of the evaporation, to grasp the flask in a holder and manipulate it over a free flame, by turning and twisting, so as to heat every part of the flask, until complete dryness is attained.

4. As soon as the flask is sufficiently cool, add 35 cc. of a prepared ammoniacal solution and heat to boiling. This solution is made by dissolving 200 grams of commercial ammonium chloride in a mixture of 500 cc. of strong ammonia (sp. gr. 0.90) and 750 cc. of water.

Boil the contents of the flask very gently for a minute or two, or until disintegration of the residue is complete (avoiding hard boiling and loss of ammonia), and then add saturated bromine water and continue the boiling for a short time.

The amount of bromine water to add depends upon the quantity of manganese apparently present, as indicated by the deep brown color of the dry residue. All the manganese is originally precipitated by the mixture of nitric acid and potassium chlorate, but on evaporating to dryness, some of the manganese is again reduced to the protoxide form and becomes more or less soluble. With ores showing little or no manganese, 10 cc. of saturated bromine water are sufficient, and 25 cc. will usually suffice in any case.

5. Filter the hot solution through an 11-cm. filter into a 400-cc. beaker. I have found that in most cases the liquid runs through much more rapidly if a small wad of absorbent cotton is first placed in the apex of the filter and wetted.

Wash out the flask with hot water. A slight adhering residue may be disregarded; a larger residue that cannot be removed with a rubber-tipped rod may be treated as follows: Add 2 or 3 cc. of strong hydrochloric acid to dissolve it, and then, without diluting the solution, add 5 cc., or an excess, of strong ammonia, and rinse into the filter. Any

traces of manganese not precipitated by the ammonia are usually negligible.

Wash the residue on the filter ten times with a nearly boiling ammonium chloride mixture, which is best contained in a wash-bottle of the type described on page 8, but a small beaker will serve. To make the ammonium chloride mixture, dissolve 100 grams of commercial ammonium chloride in water, add 50 cc. of strong ammonia and dilute to 1 liter.

6. Add a little litmus solution to the filtrate as an indicator, and then cautiously neutralize with strong hydrochloric acid. Be very particular with the neutralization and then add 3 cc. of hydrochloric acid in excess. When there is sufficient copper present to act as an indicator, the litmus may be dispensed with.

Dilute the liquid, if necessary, to about 250 cc., with hot water, heat nearly to boiling and then add 50 cc. of saturated hydrogen sulphide water. The mixture is now ready for titration. If the final bulk of the liquid happens to be considerably larger than prescribed it will have no material influence on the zinc result.

Pour about one-third of the hot liquid into a beaker as a reserve and conduct the titration as described for the standardization of the ferrocyanide, adding portions of the reserve as the end-point is successively passed.

In correcting for the final reading of the burette, it is usually sufficient to deduct for as many tests as show a brown tinge and one drop additional. This is shown by running a blank test, adding the ferrocyanide, one drop at a time, and making a test after each drop. In the course of a minute a brown tinge will show in all the tests except the first. The usual total correction is 0.25 cc.

Multiply the number of cubic centimeters used by the percentage value of 1 cc. to obtain the per cent of zinc in the ore.

7. Ordinarily, any sulphides precipitated by the hydrogen sulphide water need not be filtered off, as the discoloration produced by even 10 per cent of copper, for instance, does not too badly mask the uranium test. With a large amount of copper present the procedure may be as follows: After adding an excess of 3 cc. of strong hydrochloric acid to the filtrate and diluting it to about 200 cc. with hot water, pass in hydrogen sulphide gas to saturation. Filter through an 11-cm. filter and wash the precipitate thoroughly with hot water. If a little copper oxidizes and runs into the filtrate it will do no harm, as it is

immediately re-precipitated as sulphide. Heat the filtrate, which should have a final volume of about 250 cc., nearly to boiling, and titrate as usual.

8. **Notes.**—*a*. It is not sufficient to wash the residue of ferric hydroxide, etc., simply with hot water. An appreciable amount of zinc is likely to be retained unless the residue is thoroughly washed with the hot ammoniacal solution prescribed. A direct test with a 40 per cent zinc ore showed a retention of 1.27 per cent, which was afterward easily washed out with the ammoniacal solution.

b. The use of granulated test lead as a precipitant for copper is not recommended. Lead acts more slowly than hydrogen sulphide, sometimes fails to entirely remove the copper, and, unless the precaution of a special procedure be adopted, will always produce a solution with an unknown and variable degree of acidity, thus influencing the end-point. For a method using test lead see 11.

c. Metallic aluminum appears to be entirely unsuitable for precipitating the copper, unless the aluminum which goes into solution is subsequently removed. Aluminum salts affect the titration and produce incorrect results. In carefully conducted experiments I have always found this to be the case, under my usual working conditions.

d. Even when the zinc contents of a solution are approximately known, it is not advisable, in the titration, to omit working with a reserve portion and proceeding in the regular manner. The reaction between the ferrocyanide and the zinc may be varied, at least temporarily, by varying the conditions, and a false end-point may be obtained by working too rapidly. A false end-point may be recognized by noting that the addition of a few more drops of ferrocyanide does not increase the intensity of the test. By continuing to add ferrocyanide, the color of the test will finally disappear, and will then return only when the true end-point is reached.

e. Cadmium is not completely precipitated by hydrogen sulphide from a hydrochloric acid solution containing considerable alkali chloride. In the regular method (and likewise the alternate and test-lead methods), therefore, cadmium is to a greater or less extent counted as zinc,[1] small amounts not being precipitated at all by the hydrogen sulphide.

f. Arsenic, when present in large amount, may make trouble by retaining iron in the ammoniacal solution filtered from the residue. No attention need be paid to arsenic unless its presence in excess is

thus indicated. In such a case begin anew and give the ore the following preliminary treatment: Dissolve the ore in the usual way, but use an 8-oz. copper flask instead of an Erlenmeyer. Boil the solution nearly to dryness, then add 10 cc. of strong hydrochloric acid and boil until it is half gone (to expel nitric acid). Now add about 4 cc. of a solution of 1 gram of sulphur in 5 cc. of bromine and boil gently for a few moments. Then add 4 cc. of strong sulphuric acid and boil, by manipulating the flask over a free flame, until it is nearly all driven off. The arsenic will thus be sufficiently expelled. Cool, add 10 grams of ammonium chloride and 20 cc. of water and finish the assay as described in 9.

g. The opinion seems to be very common that gelatinous silica, unless well dehydrated, is liable to combine with and retain some of the zinc on the addition of the ammoniacal extraction solution. My own experiments have invariably indicated that this is not the case. A large amount of gelatinous silica may hold some zinc mechanically and thus render its complete extraction and the thorough washing of the residue more difficult. The partial dehydration obtained by following the regular method is usually quite sufficient to overcome this trouble. When hydrofluoric acid has been used in the decomposition of the ore no appreciable amount of gelatinous silica is likely to be found.

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[1] Zinc is precipitated by potassium ferrocyanide from acid solutions, not as a straight zinc ferrocyanide, but as a zinc potassium ferrocyanide, the formula of which may be expressed as follows: $K_2ZnFe(CN)_6.Zn_2Fe(CN)_6$. The formula of potassium ferrocyanide is $K_4Fe(CN)_6$, and an inspection of the previous formula shows that 2 molecules of potassium ferrocyanide are required to precipitate 3 atoms of zinc. The formula of the crystallized potassium ferrocyanide is $K_4Fe(CN)_6+3H_2O$, and the molecular weight is 422.366. Two mol. = 844.732. Three atoms of Zn = 196.11. One per cent of zinc, on the basis of 0.5 gram of ore taken for analysis, = 0.005 gram. The amount of crystallized ferrocyanide required to be in 1 cc. in order that 1 cc. = 1 per cent of Zn, may now be found from the following proportion: 844.732 : 196.11 = x : 0.005. x = 0.02154. This is 21.54 grams per liter.

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9. Alternate Method.—I have observed that in the presence of a large excess of ammonium chloride, ammonia will precipitate iron entirely free from zinc. This fact may be applied to the assay of an ore as follows:

Treat 0.5 gram in an 8-oz. copper flask with 5 cc. of strong hydro-

chloric acid and 10 cc. of strong nitric acid and boil to pastiness. The final use of 5 cc. of strong sulphuric acid is advisable if gelatinous silica separates. In this case boil until the sulphuric acid is nearly gone—best by manipulating the flask over a free flame. Cool sufficiently, add 10 grams of ammonium chloride and 20 cc. of water and boil the mixture to effect solution of everything soluble. If basic salts remain, add a few drops of hydrochloric acid to dissolve them. When the solution is clear, remove from the heat, add strong ammonia water in about 5 cc. excess, then 20 cc. of saturated bromine water and boil for a few minutes. If the blackish-brown color of the precipitate indicates much manganese, add more bromine water to insure its complete precipitation, and again boil. In doubtful cases test the filtrate with bromine water. Filter and finish as in the regular method (6).

10. Particular pains must be taken to remove all manganese with the bromine water, since none is separated during the decomposition, as in the regular method. When the amount of manganese present is in excess of a few per cent it is not safe to precipitate it with bromine, since it is liable to carry down an appreciable quantity of zinc as manganite (MANGANESE, 13). In such a case I should not advise the use of the alternate method.

11. **Method Using Test-lead to Precipitate Copper.***—Begin as in the regular method, (3). Use hydrogen peroxide (6 cc. or more) instead of bromine water to precipitate the manganese. (Bromine and its compounds are more difficult to subsequently remove.) Boil for several minutes to expel the excess of peroxide. Filter and wash as usual. Make the filtrate very slightly acid with hydrochloric acid, using methyl orange as indicator. Add about 20 grams of granulated test-lead, cover the beaker, and boil until all the copper is precipitated, i.e., until the solution has become perfectly colorless and then a little longer. Dilute with hot water to about 250 cc., add 3 cc. of strong hydrochloric acid and 1 cc. of a 50 per cent solution of sodium thiosulphate, and titrate as usual at an initial temperature of about 85° C., using the uranium indicator and making the proper deductions as in the regular method.

To standardize the ferrocyanide solution, dissolve about 0.200 gram of zinc in 10 cc. of 1 : 2 hydrochloric acid, add 7 grams of ammonium chloride, make alkaline with ammonia and then reacidify

* Method used by Mr. Chas. S. Curtis, U. S. Assayer, in the U. S. Customs Assay Office, Kansas City, Mo.

slightly with hydrochloric acid, using methyl orange as indicator. Add 3 grams of test-lead, heat to boiling, dilute to about 250 cc. with hot water, add 3 cc. of strong hydrochloric acid and 1 cc. of a 50 per cent solution of sodium thiosulphate and titrate as just described.

12. Treatment of Refractory Ores, etc.—No exact line of treatment can be prescribed for this class of material. The following will usually suffice: Begin according to the regular method (3). As soon as decomposition is as complete as possible, dilute somewhat and filter from the insoluble residue, washing the latter with hot water. Receive the filtrate in an 8-oz. Erlenmeyer flask and allow it to concentrate considerably while treating the residue. If the residue is likely to contain lead, wash it next with the hot sodium acetate solution used in the lead assay (LEAD, 1), and then thoroughly with hot water to remove the sodium acetate, rejecting these filtrates. Ignite the washed residue at a low temperature in a platinum dish to remove the filter paper. Cool, add equal parts of strong hydrochloric and hydrofluoric acids, and digest on a water-bath until solution is complete, adding more acids if necessary. Finally, evaporate to small bulk and then add more hydrochloric acid and evaporate again to small bulk to remove most of the hydrofluoric acid. Wash this solution into the main portion which is concentrating. Boil the combined solutions to small bulk, add 10 cc. of strong nitric acid and boil nearly to dryness. Now add 12 cc. of strong nitric acid and 5 grams of potassium chlorate and continue as in the regular method.

Sometimes the ore or other material may be treated at the outset with hydrochloric and hydrofluoric acids, in platinum, as just described for the residue.

The washed insoluble residue may also be fused with alkali carbonate, either alone or mixed with borax glass, the melt disintegrated with water, and the mixture transferred to the flask containing the main solution, finishing as above.

13. Modification to Avoid Cadmium.—If it be desired to avoid the influence of cadmium, the following method may be adopted:

Begin by either the regular or the alternate method, and proceed as usual until the filtered ammoniacal solution is obtained. To this filtrate add about 3 grams of potassium cyanide, allow to dissolve and then add 10–15 cc. of strong hydrogen sulphide water. A sufficient quantity to precipitate any possible cadmium or lead is all that is necessary. Stir the mixture to make sure of the solution of zinc

sulphide, and then allow to stand a short time for the cadmium sulphide to separate and settle. Copper and zinc go into solution while cadmium and lead sulphides are precipitated. Without, at the outset, unduly disturbing the precipitate, which is likely to clog the filter, filter through an 11-cm. filter into a 400-cc. beaker. Re-filter the first portions if not clear. Wash out the beaker with cold water and then wash filter and precipitate thoroughly with a cold 2 per cent solution of potassium cyanide.

Remove the filtrate to a hood, drop in a piece of litmus paper and acidify with strong hydrochloric acid in about 5 cc. excess. Add about a gram of potassium chlorate, cover the beaker and boil until the hydrocyanic acid is expelled and the mixture has clarified. Finally remove from the heat, add a little litmus solution, neutralize with ammonia, and then reacidify with 3 cc. excess of hydrochloric acid. Have the volume of the solution about 200–250 cc.

To the nearly boiling liquid add 50 cc. of strong hydrogen water and titrate as usual.

Ordinarily, the very small amounts of cadmium in zinc ores may be counted as zinc, but the occasion sometimes arises where a separation is required.

14. Waring's Zinc Method.—This method depends upon the separation of the zinc from manganese, iron, and aluminum by means of hydrogen sulphide, under slight pressure, in a solution very slightly acidified by formic acid, the metals of the copper group having been previously separated by metallic iron or aluminum with simultaneous reduction of ferric salts. The operations are:

(1) *Solution.*—The calamine, willimite, franklinite, blende, and other soluble minerals, or ores containing them, are decomposed by hydrochloric acid or aqua regia, with subsequent treatment and evaporation with an excess of hydrochloric or sulphuric acid to thoroughly eliminate nitrous compounds. If zinc spinels or aluminates are present, the insoluble residue must be fused with a mixture of sodium carbonate and borax glass, the fused mass dissolved and the solution added to the main one. If much silica is present, spinels are decomposed by fusion with sodium carbonate in a platinum crucible, any lead sulphate present having been extracted by ammonium acetate. In the absence of silica or boric acid, the spinels cannot be decomposed by fusion with sodium carbonate alone. In such a case they can be decomposed by prolonged fusion with an alkali bisulphate. Sil-

icates, such as cinders from oxide furnaces, unchilled slags, and some natural silicates undecomposable by acids, must be fluxed or sintered with sodium carbonate before treatment with hydrochloric acid. It is not necessary, in any case, to evaporate to dryness to separate silica—it can be filtered off in the gelatinous state. This can be done very rapidly, after dilution with water, when the gelatinization has reached a maximum and before dehydration has begun. The gelatinous silica at this stage will not retain any traces of metals after a few washings.

(2) *Reduction.*—To avoid the effects of reactions like

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S,$$

and at the same time to remove copper, silver, and bismuth before precipitating with hydrogen sulphide, the filtered solution, made fairly acid with hydrochloric or sulphuric acid, is boiled for fifteen or twenty minutes with a strip of clean sheet iron or steel. By this treatment all the metals likely to be precipitated with zinc as sulphides are separated, except cadmium, which is not in the least degree reduced by metallic iron.

Mr. G. C. Stone has suggested the use of metallic aluminum for the reduction. This has the advantage of separating cadmium and lead along with the other metals of the copper group, since both are completely precipitated by aluminum from a rather strongly acid boiling solution of sulphates or chlorides, so that when zinc only is to be determined, the subsequent operations are very much shortened.

Reduction may also be effected by means of sodium sulphite or thiosulphate, when copper, or copper and aluminum are to be determined from the same weighed portion.

The reduction is followed by filtration, the filtrate being received in a flask of about 300-cc. capacity.

(3) *Neutralization.*—Add to the filtrates a drop of methyl orange, then run in, from a pipette, a rather dilute solution of sodium hydroxide, meanwhile constantly agitating the contents of the flask with a swirling motion, until the pink color barely, but permanently, changes to a light yellowish tint, and the cloudiness, due to the separation of hydroxides, fails to clear up entirely. Then add, drop by drop, enough 50 per cent formic acid (sp. gr. 1.12) to just restore the permanent pink color, and add up to half a cubic centimeter additional. Dilute the solution

to 200 or 250 cc. (or so that it will contain not more than 0.15 to 0.20 gram of metallic zinc in 100 cc.) and heat to about 80°.

(4) *Precipitation.*—A rubber stopper, through which passes the delivery-tube from a source of supply of hydrogen sulphide,* is loosely placed in the neck of the flask and a moderately rapid stream of gas allowed to pass through the hot liquid. When the precipitation of zinc sulphide is well under way, the stopper is pushed in tightly. Absorption of the gas ceases when all the zinc is precipitated; the precipitate settles quickly, and the gas pressure rises rapidly when the operation is completed. When several precipitations are to be made at the same time, the flasks are arranged in succession in the usual manner and the first is removed when the precipitation is well started in the third, and so on, changing the gas connections as required. The outlet from the last flask is not closed until the precipitation is partially completed therein. Numerous experiments have shown that zinc can be completely precipitated and separated from iron, manganese, and alumina under the conditions named, by the passage of only a very little more than the amount of hydrogen sulphide theoretically required. The use of a large excess is therefore unnecessary and is also undesirable.

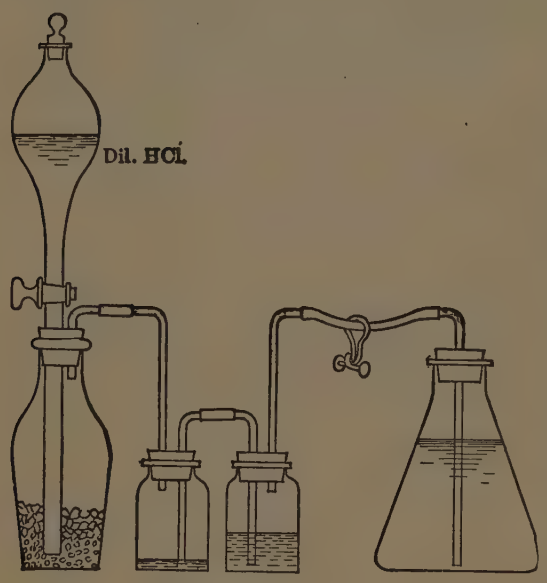

FIG. 20.

(5) *Treatment of the Precipitate.*—When the preceding operations have been properly performed, the precipitated zinc sulphide will be pure white, pulverulent, and very easily filtered and washed. Hot water only need be used for washing, no zinc will dissolve or pass through the filter, as is the case with the slimy zinc hydrosulphide precipitated from cold solutions in the usual manner. Pour the contents of the flask upon a filter at once and wash with hot water. Spread the filter with its contents upon a large watch-glass or on the

* The apparatus used by Waring is shown in Fig. 20. It is adapted from that of C. A. Brewer. The lower end of separatory-funnel is somewhat contracted and extends to bottom of coarse shot upon which rests the FeS.

inner wall of a capacious beaker, and wash the precipitate into the bottom of the beaker by a jet of hot water. Wash the precipitating-flask and the lower end of the gas delivery-tube with 10 cc. of strong hydrochloric acid, followed by hot water, pouring the acid and washings successively over the washed filter on to the precipitate in the beaker. When the volume of the acid solution has reached 125 to 130 cc., the solution is warmed gently to dissolve the zinc sulphide completely.

When cadmium is also present (i.e., when the reduction has been effected by metallic iron), the zinc sulphide will dissolve completely before any cadmium sulphide is dissolved. By practice and experience, the point when all the zinc is dissolved and only the brilliant yellow cadmium sulphide remains, can easily be distinguished. The solution is then further diluted with an equal volume of hydrogen sulphide water, allowed to settle and the cadmium sulphide filtered off and estimated in the usual way by warming with acid ferric sulphate and titrating with permanganate. The iron equivalent of the permanganate used, multiplied by 1.006, equals the cadmium. When the determination is properly performed, the result is accurate * (Waring).

The solution of zinc sulphide in dilute hydrochloric acid is heated to 60° or more and made up to 200 or 250 cc. with hot water; a little ammonium chloride is added, and it is ready for titration with ferrocyanide (see **6**).

Note.—The solution at this stage contains in the neighborhood of 10 cc. of strong hydrochloric acid. I would advise reducing the the excess to 3 cc. After the ZnS has been dissolved, as above, boil off the H_2S, add litmus solution, make slightly alkaline with ammonia and then reacidify with hydrochloric acid in 3 cc. excess. Now dilute, heat and titrate as in **6**. A. H. L.

The method of separating zinc by hydrogen sulphide from nickel, cobalt, and manganese, recommended by Fresenius,† is not applicable when iron is present, as iron is thrown down by hydrogen sulphide in the presence of sodium acetate.

* Treadwell says (Anal. Chem., Hall, 2d Ed., II, p. 167): "It is not possible to precipitate pure cadmium sulphide from acid solutions by means of hydrogen sulphide; the precipitate is always contaminated with a basic salt ($Cd_2Cl_2S-Cd_2SO_4S$, etc.), whether the precipitation takes place in cold or hot solutions, whether under atmospheric pressure or under increased pressure (in a pressure-flask), and in fact the amount of basic salt formed increases with the amount of free acid present."

† American edition, sec. 160, paragraphs 74 and 75.

15. Modification. For Low-grade Zinc Ores, Slags, Furnace Residues, etc., and for all purposes wherein it is required to determine small amounts of zinc accurately.

Proceed exactly according to the method just described until the zinc sulphide precipitate has been washed; then, instead of dissolving the precipitate, dry and ignite it carefully in a clean muffle without separating it from the paper. No loss of zinc will occur, nor will basic sulphate be formed, if the wet precipitate is ignited at the mouth of the muffle until the paper is consumed, and the oxidation of the residue is then conducted at a low temperature (about 450°) until at the last, when it may be moved back to where the temperature is near the melting-point of silver.

As much as 0.15 gram of zinc sulphide can be completely oxidized in this way in forty to sixty minutes. The calcination may be effected in a smooth shallow scorifier, an inch and half in diameter, from which the calcined oxide can be brushed into the scale-pan without appreciable loss. Calculate the zinc from the ZnO found by multiplying by 0.8034.

Waring's method has been modified both by its author and by Dr. H. C. Weber of the U. S. Bureau of Standards, and the following scheme, including the changes, is proposed by the Zinc Committee of the American Chemical Society.

16. Modified Waring Method.*—After the weighed sample has been decomposed by acids alone, or aided by fusion, as the case may require, all the zinc is to be brought into solution as sulphate. If nitric acid was used in the decomposition, all traces of it must be expelled by evaporation with hydrochloric and sulphuric acids successively, or by two evaporations with sulphuric acid, finally to abundant evolution of SO_3 fumes. Dissolve the mass in 25 to 40 cc. of water and add sufficient sulphuric acid to bring the free acid in the solution up to 10 or 15 per cent. Introduce a piece of heavy sheet aluminum and boil ten minutes, or to complete reduction. Filter, and wash through a filter containing a piece of aluminum into a beaker containing a stirring-rod or strip of the same metal; cool, add a drop of methyl orange, and neutralize carefully with *sodium bicarbonate* to a light straw color. Add, dropwise, dilute formic acid (20 per cent strength) until the pink color is just restored, then 5 drops more. (Dilute hydrochloric acid, 1 part strong acid to 6 parts water, may be

* Jour. Am. Chem. Soc., XXIX, 265.

substituted for formic acid when ammonium thiocyanate * is to be introduced.) Dilute to about 100 cc. for each 0.1 gram of zinc possibly present, add, if much iron is present, 2 to 4 grams ammonium thiocyanate, remove the strip of aluminum, heat nearly to boiling, and saturate with hydrogen sulphide. Allow the pure white zinc sulphide to subside for a few minutes, then filter and wash with hot water. Transfer precipitate and filter to a capacious beaker, heat with 8 to 10 cc. of strong hydrochloric acid and 30 or 40 cc. of water, until the zinc is all in solution. Determine the zinc as pyrophosphate, containing 42.88 per cent zinc, or by titration with ferrocyanide. The use of ammonium heptamolybdate † in 1 per cent solution as an indicator, instead of uranium acetate or nitrate, is recommended, provided all free hydrogen sulphide has been previously expelled from the solution by heating. If a blue color still appears in the test drop, add a crystal or two of sodium sulphite to the zinc solution, to decompose any remaining hydrogen sulphide.

17. Notes.—Using the thiocyanate modification and the ferrocyanide titration, I have found the above very accurate, except that cadmium was not entirely removed—at least in presence of copper. To conform to my method of standardization, proceed as follows: Drop filter with zinc sulphide into a 6-oz. flask. Cleanse beaker and delivery tube with 25 cc. of hydrochloric acid and rinse into the flask. Boil to dissolve the zinc, disintegrate the filter and expel all hydrogen sulphide. Add a little litnus solution or paper, neutralize with ammonia, and then reacidify with 3 cc. excess of hydrochloric acid. Transfer to a 400-cc. beaker, dilute to 250 cc. and titrate hot, as usual (**6**).

18. Notes by Waring and Stone.—Under the conditions described, the precipitation of cadmium is complete, but traces of copper remain in solution unless the boiling is continued for a very long time; this prolonged boiling is not necessary, as the copper is afterwards precipitated as sulphide with the zinc and does not redissolve with the latter.

In neutralizing, if the solution is strongly acid, it is better to nearly neutralize with sodium or potassium hydroxide and finish with bicarbonate. This not only saves time but lessens the chance of loss by foaming.

It is not necessary to pass the hydrogen sulphide under pressure

* Zimmermann, Ann. Chem., (Liebig), 99, 1.

† Nissenson and Kittembeil, Chem. Zeit., 77 (1905), 951–955.

if the solution is diluted as already directed. The gas should be passed through the solution until a drop of the liquid blackens a drop of cobalt or nickel sulphate or chloride made alkaline with ammonia. After a little experience it is not necessary to make even this test. It is very important that the zinc solution should be quite hot during the precipitation of the sulphide; therefore it is advisable to begin nearly at the boiling-point and to pass the gas rapidly. If the heating of the solution has taken much time, the excess of formic acid may volatilize (if this reagent has been used). In such cases formic acid must again be added, in sufficient quantity, to make the solution acid.

We most strongly recommend that zinc be determined gravimetrically by weighing as pyrophosphate, except where the operator has had much and recent practice with the ferrocyanide titration. While the latter is capable of giving very accurate results it will only do so when *all* the conditions are *exactly* the same both in standardizing and during the final titration, and it is necessary to have considerable experience with the method to be sure of accuracy.

19. Weighing the Zinc as Pyrophosphate.*—Filter the solution of the zinc sulphide in hydrochloric acid finally obtained in Waring's Method and bring the filtrate to a cold, dilute and slightly acid condition. Now add a *large* excess of ammonium sodium hydrogen phosphate and then neutralize very carefully with ammonia, adding it drop by drop, finally adding a drop or two in excess. Finally, add about 1 cc. of acetic acid and warm gently until the flocculent precipitate of $ZnNH_4PO_4+H_2O$ has settled completely as a dense crystalline powder, Filter and wash with hot water.

Dry the filter and precipitate, separate the paper and burn it, add the ash to the residue and ignite the two, gently at first, then for a few minutes at a bright-red heat. Cool and weigh as $Zn_2P_2O_7$, containing 42.88 per cent of zinc.

The flocculent $ZnNH_4PO_4+H_2O$ is very soluble in the mineral acids as well as in ammonia, but after crystallization it is much less soluble in the latter. It is only slightly soluble in acetic acid; an excess of 1 cc. in 100 cc. of solution does not dissolve an appreciable quantity. It is somewhat soluble in all ammonium salts, if only a small excess of phosphate is present. The addition of 1 cc. of a 10 per cent solution of sodium ammonium phosphate for each 0.005 gram of zinc is sufficient to entirely prevent its solution in ammonium

* Method of Geo. C. Stone. W. Geo. Waring, Jour. Am. Chem. Soc., XXVI, 28.

chloride or sulphate or in the acetate unless the latter is present in enormous quantity. It is, however, always slightly soluble in the oxalate. Therefore, for very accurate work, lime and magnesia, if present in the zinc solution, are preferably separated together as phosphates, after adding a large excess of ammonia and reprecipitating; then the combined filtrates are to be slightly acidulated and proceeded with as above. The crystalline zinc ammonium phosphate is quite insoluble in hot or cold water.

CHAPTER XXXI

COMBINING DETERMINATIONS

It is an ordinary occurrence for the technical chemist to have to determine several constituents in the same sample of ore. The expert operator will, of course, be able to combine his regular methods for single constituents, whenever possible or convenient, so as to make two or more determinations from the same weighed portion of ore, and thus save considerable time. The accuracy of the work is sometimes lessened by such a combination and its adoption will then depend upon the rigor of the requirements.

The following examples are perhaps sufficient to show how work can be hastened in a busy laboratory, using only technical methods. Of course, by the tedious operations of exact analysis, many constituents can sometimes be determined from the same weighed portion, but such methods are not under consideration. Where much extra manipulation is involved, it is usually not worth while to work by a combination method.

1. **Copper, Lead and Insoluble.**—Make the copper as usual (Copper, 6), but take the precaution to cool the solution before the first filtration and to wash the lead sulphate residue with dilute sulphuric acid. Dissolve the lead sulphate on the filter with the usual hot sodium acetate solution and proceed with the filtrate as described for lead (Lead, 6). Thoroughly wash the residue remaining on the filter with hot water, to remove the sodium acetate, and then ignite filter and contents and weigh as insoluble residue.

2. **Zinc, Iron and Insoluble.**—Make the zinc as usual (Zinc, 3).* The iron and insoluble residue will be either on the filter or adhering in the flask. Rinse the precipitate on the filter into a beaker with hot water, using as little as possible. Add 5 cc. of strong hydrochloric acid and warm the mixture until the ferric hydroxide, etc., has dis-

* Of course, the use of hydrofluoric acid would vitiate the insoluble residue determination.

solved. Transfer this solution, and any insoluble residue, into the original flask and again warm, if necessary, to dissolve any adhering precipitate. Now filter through the same filter as before, thus dissolving any precipitate thereon, receiving the filtrate in an 8-oz. flask. Wash flask and filter with hot water acidulated with a few drops of hydrochloric acid, and see that all the residue is transferred from the flask to the filter, using a rubber-tipped bent glass rod, if necessary, to detach adhering particles. Concentrate the filtrate by boiling, if too bulky, and determine the iron in it as usual (IRON, 29).

The insoluble residue is now ready to ignite unless it is likely to contain lead. In this case dissolve out the lead with a strong hot solution of ammonium chloride, acidulated with hydrochloric acid, or employ the hot sodium acetate solution used in the lead assay (LEAD, 1). Finally, wash thoroughly with hot water, then ignite filter and contents and weigh as usual.

3. **Calcium and Magnesium.**—It is evident that no modifications of the methods described are necessary in this case. Simply proceed as for CaO (CALCIUM, 1), and in the filtrate from the calcium oxalate determine the MgO in the usual manner (MAGNESIUM, 1, 2).

4. **Insoluble, Iron, Calcium and Magnesium.**—Proceed for insoluble residue by any appropriate method (SILICA, 1). Wash the filtered residue with hot water slightly acidulated with hydrochloric acid and then treat it as in 2 above. If it requires purification from lead, do not add the resulting filtrate to the original filtrate.

Proceed with the original filtrate as for calcium (CALCIUM, 1), and thus obtain the iron as ferric hydroxide, the calcium and magnesium being in the filtrate (or filtrates). Determine the latter as above (3).

If the ferric hydroxide is small in amount, dissolve it on the filter by pouring over it a hot mixture of 10 cc. of strong hydrochloric acid and 20 cc. of water, receiving the filtrate in an 8-oz. flask. It is best to wash larger amounts into a beaker with a little hot water, add 5–10 cc. of hydrochloric acid and warm until the iron precipitate has dissolved, pouring the solution through the filter to dissolve what remains there. Wash the filter with hot water slightly acidulated with hydrochloric acid. Concentrate the filtrate by boiling, if necessary, and determine the iron in it in the usual manner (IRON, 29).

6. **Copper and Iron.**—Proceed as for copper by the iodide method (COPPER, 6), determining the copper as usual. The filtrate from the precipitated copper will contain the iron all reduced, but also contain-

ing hydrogen sulphide. Boil the solution in a flask until the hydrogen sulphide is completely expelled, then transfer it to a battery-jar containing some cold water, dilute to 700 cc. with cold water, add 5 cc. of strong sulphuric acid and titrate with permanganate, as described in IRON, 8. Of course, the aluminum used should be practically free from iron.

It will be observed that the above combinations can be combined with each other in certain cases, as in the example which follows:

7. **Insoluble, Lead, Copper and Iron.**—Proceed as in 1, determining the lead and insoluble in the residue, and then determine the copper and iron in the filtrate according to 6.

CHAPTER XXXII

BOILER WATER

FULL directions for the analysis of water to be used for steam purposes can be found in most of the books on technical analysis, and it is not intended to describe an elaborate method in this work. The following scheme can be carried out very quickly, and is sufficiently accurate in most cases:

If the water is turbid, allow it to settle, or filter it so as to remove the suspended matter.

1. **Total Solids.**—Evaporate 100 cc. in a weighed platinum dish on the water-bath to dryness. If the dish is too small to hold 100 cc. at once, measure the water into a beaker and transfer it to the dish as the evaporation proceeds. A 100-cc. pipette is most convenient for the measuring, as no washing out is necessary and there is, therefore, no wash-water to evaporate. After evaporation place the dish and residue in an air-bath and heat at 150° C. for thirty minutes. Cool in desiccator and weigh.

2. **Organic and Volatile Matter.**—Hold the dish containing the dry residue in the tongs and manipulate it over a Bunsen flame so as to burn off the organic matter at as low a temperature as possible. Sometimes the burned residue remains dark, owing to the presence of manganese. If this is mistaken for unburned carbon, too high a temperature may be employed in attempting to consume it and more or less carbon dixoide may be expelled from carbonates in consequence. This carbon dioxide can be replaced by adding a little CO_2 water and evaporating to dryness, but it is hardly worth while to take this extra trouble, as the possible errors of this determination are liable to make it unsatisfactory in any event. The result obtained is seldom used, but it sometimes proves useful as a check. After the ignition cool the dish in a desiccator and weigh, noting the loss from the last weight.

3. **Conversion to Sulphates.**—Acid sufficient dilute sulphuric acid to the last residue in the dish (a few drops are usually enough)

and turn the latter in various positions so that the acid will come in contact with all the residue. Note whether or not an effervescence indicating carbonates, is produced, as knowledge on this point may prove useful later. Heat the dish cautiously so as to expel the water and free sulphuric acid and then raise the temperature sufficiently to decompose any iron sulphate and leave ferric oxide; avoid unnecessary overheating however. Cool and weigh as combined Na_2SO_4, $CaSO_4$, $MgSO_4$, Fe_2O_3, and SiO_2. This weight will be used in the calculation of results.

4. **Silica.**—Warm the sulphate residue with sufficient dilute hydrochloric acid to dissolve all the sulphates. If there is much ferric oxide it is best to warm with a little strong acid at first until it has dissolved. Filter through a small ashless filter and wash with hot water. Sometimes it is a good plan to loosen any insoluble matter on the sides of the dish with a rubber-tipped glass rod and continue the heating with dilute acid to make sure that all sulphates are dissolved. Return the filter and any insoluble residue to the dish and ignite. After cooling, weigh as SiO_2.

5. **Ferric Oxide, etc.**—Heat the filtrate from the silica nearly to boiling and add a slight excess of ammonia, preceded, if it is possible that manganese is present, by 5 cc. of strong bromine water. Bring to a boil and then allow to stand over a low flame for a short time, for the precipitate to collect. Finally, filter through a small ashless filter, wash with hot water, ignite and weigh, after cooling, as Fe_2O_3. The amount is usually so small that the platinum or porcelain crucible used for the ignition need not be weighed, but the ferric oxide may be transferred directly to the scale-pan. Only in rare cases where Mn_3O_4 or Al_2O_3 are present in unusual amount, it is necessary to make any special separation of these substances.

6. **Calcium Oxide.**—Heat the filtrate from the ferric hydroxide to boiling, add sufficient ammonium oxalate solution and allow to stand, hot, till the precipitate has settled. Filter, wash well with hot water, and determine the CaO in the calcium oxalate by titration with potassium permanganate, as in CALCIUM, 4.

7. **Magnesium Oxide.**—Concentrate the filtrate from the calcium oxalate to smaller bulk if necessary, and then precipitate the magnesium as magnesium ammonium phosphate, as described in MAGNESIUM, 2, finally weighing as $Mg_2P_2O_7$ and calculating to MgO.

8. **Alkalies.**—For the purposes of this analysis it is usually suf-

ficient to regard the alkalies as consisting wholly of Na_2O. The amount of Na_2O is determined by calculation as follows: From the weight of the combined sulphates, etc., as determined in **3**, subtract the calculated weights of the calcium and magnesium sulphates, and also the Fe_2O_3 and SiO_2. Consider the remainder as Na_2SO_4 and calculate from it the corresponding weight of Na_2O.

For use in these calculations the table on page 279 is appended.

9. Sulphur Trioxide.—Slightly acidify 100 cc. of the water with hydrochloric acid, heat to boiling and slowly add an excess of barium chloride solution. Continue as described in SULPHUR, **1**, finally weighing the precipitated $BaSO_4$, from which the SO_3 may be calculated. $BaSO_4 \times 0.3427 = SO_3$.

10. Chlorine.—Measure 100 cc. of the water into a clean porcelain dish or casserole and determine the chlorine volumetrically by Mohr's method, described in CHLORINE, **1**. Instead of N/10 solution of silver nitrate, it is better to prepare a solution containing 4.799 grams of $AgNO_3$ per liter. One cubic centimeter of this solution will equal 0.001 gram of chlorine.

11. By the scheme as described, three portions of water, of 100 cc. each have been required in making all the necessary determinations. Considerable time may be saved,with perhaps some loss of accuracy, by using a separate portion for determining the Fe_2O_3, CaO, and MgO, instead of waiting for the residue obtained by evaporation. The error in this plan will be mainly due to the failure to remove silica, possibly causing slight increases in the results for Fe_2O_3 and MgO. In most cases, however, this error is so trifling as to be negligible. When this method is adopted do not fail to acidify the water at the outset with 5 cc. of strong hydrochloric acid, so that the subsequent addition of ammonia will form sufficient ammonium chloride to prevent the precipitatation of any calcium as carbonate.

12. Calculation of Results.—In combining the acids and bases only an arbitrary rule can be followed, and even this is subject to modification in special cases according to the judgment of the analyst. In general proceed as follows:

Combine the chlorine with sodium. If there is an excess of chlorine combine it with calcium, then with magnesium.

If there is an excess of sodium, combine it as Na_2O with SO_3. If the SO_3 is insufficient for all the available Na_2O, calculate the excess of the latter to Na_2CO_3.

If SO_3 is in excess combine it with CaO and then with MgO. Calculate any excess of CaO or MgO to $CaCO_3$ and $MgCO_3$.

Calculate the Fe_2O_3 to $FeSO_4$ if any SO_3 remains after satisfying the other bases, otherwise to $FeCO_3$. It will be observed that the iron is regarded as being in a ferrous condition. This is because organic matter is usually present. If of sufficient importance, the proper qualitative tests may be made to determine the condition of the iron.

The silica is usually reported as SiO_2, although in water containing much sodium carbonate it may exist as sodium silicate. I have observed cases where such a combination was apparently necessary to satisfy the conditions.

It will be observed that the amount of carbon dioxide is obtained entirely by calculation. In the majority of cases this will suffice, as a fairly correct idea of the general composition of the dissolved solids is all that is required. The presence of a large amount of calcium or magnesium carbonate usually indicates the existence of free carbon dioxide, which probably forms soluble acid carbonates of the alkaline earths.

13. In this analysis it is sufficiently accurate to regard milligrams per liter as equivalent to parts per million. As each determination is made on the basis of 1/10 liter, the results in milligrams, multiplied by 10, will give the parts per million. Therefore, after each result is obtained in grams, record it in decimilligrams or parts per million, by moving the decimal point four places to the right. When the entire analysis has been calculated and tabulated in this way, subtract the sum of the constituents, except organic and volatile matter, from the total solids and call the difference organic and volatile matter. It will usually be less than the figure as actually determined, for the reasons stated above.

Finally, for technical purposes, it is customary to report the results in grains per U. S. gallon of 231 cu. in., instead of in parts per million. The conversion is easily made by means of the table on page 278.

14. **Example of Calculating Analysis of Boiler Water.**—Let us suppose the various determinations have resulted as follows, in parts per million:

Total solids	928.0
Organic and volatile matter	179.0
Sulphates, etc	934.0

SiO_2	12.0
Fe_2O_3	4.0
CaO	165.0
MgO	44.7
SO_3	246.5
Cl	60.0

All the constituents are shown except Na_2O, which is determined as follows: Calculate the CaO and MgO to sulphates by multiplying by the proper factors given in the table, and then add together the following:

$CaSO_4$	400.3
$MgSO_4$	133.5
Fe_2O_3	4.0
SiO_2	12.0
	549.8

Subtract this sum, 549.8, from the sum of the sulphates, etc., 934.0, and consider the remainder, 384.2, as Na_2SO_4. This, using the table, is equivalent to 167.7 Na_2O.

Now combine the Cl with Na. 60 Cl = **98.9 NaCl** (keeping only one decimal place). 98.9 − 60 = the Na required, or 38.9. This is equivalent to 52.4 Na_2O. Subtracting this from the original 167.7 Na_2O, there remains an excess of 115.3 Na_2O.

Combine this with SO_3. 115.3 Na_2O = **264.2 Na_2SO_4**. 264.2 − 115.3 = 148.9, the SO_3 used. Subtracting this from the total SO_3, 246.5, there remains an excess of 97.6 SO_3.

Combine this with CaO. 97.6 SO_3 = **165.9 $CaSO_4$**. 165.9 − 97.6 = 68.3, the CaO used. Subtracting this from the total CaO, 165.0, there remains 96.7 CaO excess.

Combine this with CO_2. 96.4 CaO = **172.6 $CaCO_3$**.

Calculate the remaining bases as carbonates.

44.7 MgO = **93.5 $MgCO_3$**. 4.0 Fe_2O_3 = **5.8 $FeCO_3$**.

The sum of the above results in bold type, together with the **SiO_2**, 12, = 812.9. Subtracting this from the *Total Solids*, 928.0, there remains 115.1 for the *Organic and Volatile Matter*. It will be noted that this is 63.9 less than the figure actually found after ignition, indicating that some CO_2 was driven off by the heat employed.

15. The entire analysis may now be tabulated as follows:

	Parts per Million.	Grains per Gallon.
Sodium chloride	98.9	5.77
Sodium sulphate	264.2	15.41
Calcium sulphate	165.9	9.68
Calcium carbonate	172.6	10.07
Magnesium carbonate	93.5	5.45
Ferrous carbonate	5.8	0.34
Silica	12.0	0.70
Organic and volatile matter	115.1	6.71
Total solids	928.0	54.13

The results in grains per gallon are the ones usually reported. The conversion from parts per million is quickly made by means of the table on page 278.

16. Valuation of Water from Results of Analysis.—The chemist is frequently required to give an opinion as to the value of a water for steam purposes, basing his judgment on his analysis. In this regard the following points may be considered: The principal scale-forming ingredient is calcium sulphate. Calcium and magnesium carbonates also form scale to a certain extent, especially if much calcium sulphate is present to act as a cementing agent. Much of the calcium and magnesium carbonates, held in solution by excess of carbon dioxide as acid carbonates, will tend to deposit as a sludge or mud rather than as scale, when the water is boiled.

While the other constituents ordinarily found in water are not classed as scale-forming, yet, on analysis, they are practically all found to a greater or less extent in the scale, showing that with a sufficient cementing agent they all contribute to the trouble.

A large amount of alkali carbonate in water may cause foaming or priming in the boiler, as may also much organic matter.

Free acid is, of course, corrosive and is often found in mine waters, owing to the oxidation of pyrites.

Magnesium chloride is regarded as an active corrosive agent, upon the supposition that it is decomposed in the boiler with the liberation of free hydrochloric acid. When more chlorine is present in a water (containing magnesium) than can combine with the sodium (and potassium), magnesium chloride is usually considered present.

The Union Pacific Railroad Company classifies the constituents of boiler water as follows:

Incrusting, or Scale-forming Solids:

Oxides of Iron and Aluminum,
Calcium Carbonate,
Calcium Sulphate,
Calcium Chloride (corrosive),
Magnesium Carbonate,
Magnesium Sulphate (forms scale only in the presence of calcium carbonate),
Magnesium Chloride (corrosive).

Non-incrusting Solids:

Alkali Carbonates, Sulphates and Chlorides, and Organic Matter.

The quality of a boiler water is judged as follows:

Foaming and Priming:

The amount of non-incrusting solids that a boiler water can contain, before foaming or priming will take place, is about 175 grains per gallon. The less non-incrusting solids that a given water contains, the more the water may be evaporated before this degree of concentration will be reached.

The maximum limit permissible is generally taken as 50 grains per gallon, although this would be too high unless the engine occasionally took water very much lower in non-incrusting solids. For example, in the case of an average engine, of which the boiler contains 2000 gallons and the tender 6000 gallons, after the first tender of water was used, the non-incrusting solids in the boiler would have attained a concentration of 200 grains per gallon. Therefore, in judging the foaming or priming qualities of a boiler water, the service that the engine is performing, as well as the amount of non-incrusting solids in solution, must be considered.

Scale-forming Matter:

A water containing	less than	15	grains per gallon.....	Good
"	"	"	15–20 grains per gallon.....	Fair
"	"	"	20–30 grains per gallon	Poor
"	"	"	30–40 grains per gallon.....	Bad
"	"		over 40 grains per gallon.....	Very bad

CONVERSION OF "MILLIGRAMS PER KILOGRAM" INTO "GRAINS PER U. S. GALLON" OF 231 CUBIC INCHES

Parts per Million.	Grains per Gallon.	Parts per Million.	Grains per Gallon.	Parts per Million.	Grains per Gallon.
1	0.0583	36	2.1001	71	4.1418
2	0.1167	37	2.1584	72	4.2001
3	0.1750	38	2.2167	73	4.2584
4	0.2333	39	2.2751	74	4.3168
5	0.2917	40	2.3334	75	4.3751
6	0.3500	41	2.3917	76	4.4334
7	0.4083	42	2.4501	77	4.4918
8	0.4667	43	2.5084	78	4.5501
9	0.5250	44	2.5667	79	4.6085
10	0.5833	45	2.6251	80	4.6668
11	0.6417	46	2.6834	81	4.7251
12	0.7000	47	2.7417	82	4.7835
13	0.7583	48	2.8001	83	4.8418
14	0.8167	49	2.8584	84	4.9001
15	0.8750	50	2.9167	85	4.9585
16	0.9333	51	2.9751	86	5.0168
17	0.9917	52	3.0334	87	5.0751
18	1.0500	53	3.0917	88	5.1335
19	1.1084	54	3.1501	89	5.1918
20	1.1667	55	3.2084	90	5.2501
21	1.2250	56	3.2667	91	5.3085
22	1.2834	57	3.3251	92	5.3668
23	1.3417	58	3.3834	93	5.4251
24	1.4000	59	3.4418	94	5.4835
25	1.4584	60	3.5001	95	5.5418
26	1.5167	61	3.5584	96	5.6001
27	1.5750	62	3.6168	97	5.6585
28	1.6334	63	3.6751	98	5.7168
29	1.6917	64	3.7334	99	5.7751
30	1.7500	65	3.7918	100	5.8335
31	1.8084	66	3.8501		
32	1.8667	67	3.9084		
33	1.9250	68	3.9668		
34	1.9834	69	4.0251		
35	2.0417	70	4.0834		

One U. S. gallon of pure water at 60° F., weighed in air at 60° F., at atmospheric pressure of 30 inches of mercury, weighs 58334.9+ grains. (Mason, Examination of Water.)

TABLE OF FACTORS FOR USE IN WATER ANALYSIS

Given.	Required.	Factor.	Log.	Given.	Required.	Factor.	Log.
Ca	CaO	1.3990	0.1458	Mg	$MgSO_4$	4.4949	0.6945
$CaCl_2$	CaO	0.5055	9.7037	Mn_3O_4	$MnCO_3$	1.5080	0.1782
CaO	$CaCO_3$	1.7840	0.2515	Na	NaCl	2.5420	0.4051
CaO	$CaSO_4$	2.4260	0.3849	Na	Na_2CO_3	2.3040	0.3625
$CaSO_4$	Ca	0.2944	9.4690	Na	Na_2O	1.348	0.1296
Cl	$CaCl_2$	1.5650	0.1945	NaCl	Na	0.3934	9.5949
Cl	KCl	2.1030	0.3229	NaCl	Cl	0.6066	9.7829
Cl	NaCl	1.6480	0.2171	NaCl	Na_2O	0.5303	9.7245
Cl	O	0.2256	9.3534	Na_2CO_3	Na_2SO_4	1.3410	0.1272
CO_2	Na_2CO_3	2.4080	0.3818	Na_2O	Na	0.7420	9.8704
Fe_2O_3	$FeCO_3$	1.4510	0.1615	Na_2O	NaCl	1.8860	0.2755
KCl	K_2O	0.6319	9.8006	Na_2O	Na_2CO_3	1.7100	0.2329
KCl	K_2SO_4	1.1690	0.0676	Na_2O	Na_2SO_4	2.2920	0.3601
K_2O	K_2CO_3	1.4670	0.1664	Na_2SO_4	Na	0.3238	9.5103
K_2O	K_2SO_4	1.8490	0.2670	Na_2SO_4	Na_2CO_3	0.7461	9.8728
$MgCO_3$	Mg	0.2885	9.4601	Na_2SO_4	Na_2O	0.4364	9.6399
MgO	$MgCO_3$	2.0910	0.3204	SiO_2	CO_2	0.7298	9.8632
MgO	$MgSO_4$	2.9850	0.4750	SO_3	$CaSO_4$	1.7000	0.2305
MgO	$MgCl_2$	1.3430	0.1281	SO_3	K_2SO_4	2.1760	0.3377
$MgCl_2$	MgO	0.7446	9.8789	SO_3	$MgSO_4$	1.5030	0.1771
$MgSO_4$	Mg	0.2020	9.3055	SO_3	Na_2SO_4	1.7740	0.2491

CHAPTER XXXIII

COAL AND COKE

1. THE proximate analysis of coal and coke comprises determinations for MOISTURE, VOLATILE COMBUSTIBLE MATTER, FIXED CARBON and ASH. SULPHUR and PHOSPHORUS are sometimes required in addition.

The results obtained for moisture, volatile combustible matter and fixed carbon depend to a considerable extent upon the particular plan of working adopted by the operator. While the usual methods are more or less conventional and arbitrary, there is as yet no uniform agreement as to details. The methods given below are those adopted in the report of the committee on coal analysis of the American Chemical Society.*

2. **Preparation of the Sample.**—As soon as the coal or coke is received, crush it sufficiently and quarter it down to about 100 grams. Grind this coarsely, about as fine as is possible with an ordinary coffee-mill. Transfer a portion of this sample at once to a tightly stoppered bottle for use in determining moisture.

Grind 12 to 15 grams of the remainder moderately fine and transfer to a tightly stoppered bottle for use in determinations other than moisture.

3. **Moisture.**—Dry 1 gram of the coal, uncovered, in a weighed porcelain or platinum crucible at 104°–107° C. for one hour, best in a double-walled bath containing pure toluene. Cool in a desiccator and weigh covered. Loss of toluene may be prevented by attaching a reflux condenser to the steam vent of the bath.

With coals high in moisture and in all cases where accuracy is desired, determinations must be made both with the coarsely ground and with the powdered coal. When, as will usually be the case, more moisture is found in the coarsely ground than in the powdered coal, a correction must be applied to all determinations made with the latter.

* Jour. Am. Chem. Soc., XXI, 1116.

The correction factor may be found as follows: Divide the difference in moisture by the per cent of other constituents than moisture, as found in the powdered coal. Multiply the per cent of each constituent as found in the powdered coal by the quotient, and subtract the resulting product from the amount of the given constituent.

Thus, suppose the results of an analysis give:

	Coarsely Ground Coal.	Powdered Coal.
Moisture	12.07	10.39
Volatile combustible matter	.....	34.25

then the correction factor will be

$$\frac{12.07-10.39}{100-10.39}=\frac{1.68}{89.61}=0.0187$$

and the true per cent of volatile combustible matter will be

$$34.25-(34.25\times 0.0187)=33.61.$$

4. Volatile Combustible Matter.—Place 1 gram of the fresh, undried, powdered coal in a 20- or 30-gram weighed platinum crucible having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum or pipe-stem triangle with the bottom 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find " volatile combustible matter " subtract the per cent of moisture from the loss found here.

The term " Volatile Combustible Matter " does not represent any definite compound or class of compounds which exist in the coal before heating. The method is arbitrary and the application of higher temperatures will expel more volatile matter.

(*Note.*—I have found western lignites to suffer a serious mechanical loss when subjected at once to the full heat of a Bunsen burner as directed above, the loss sometimes amounting to several per cent. To avoid this, with such coals, I proceed as follows: Heat the covered crucible over a Bunsen burner with the flame turned very low and not touching the crucible. After heating for several minutes in this man-

ner, increase the temperature very gradually and only as fast as the coal will permit without suffering mechanical loss. Finally, when the full power of the Bunsen flame is attained adjust it as directed above and continue the heating for five minutes. Cool in desiccator and weigh as usual.)

5. **Ash.**—Burn the portion of powdered coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter. It is advisable to examine the ash for unburned carbon by moistening it with alcohol.

When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of ash, and, since three atoms of oxygen replace four atoms of sulphur, the weight of the ash is less than the weight of the mineral matter in the coal by five-eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee does not recommend such a correction for "proximate" analyses. When analyses are to be used as a basis for calculating the heating effect of the coal a correction should be made.

6. **Fixed Carbon.**—This is found by subtracting the per cent of ash from the per cent of coke or residue left after expelling the volatile matter. Or, it is the difference between the sum of the other constituents determined and 100. Sulphur, which passes partly into the "volatile combustible matter" and partly into the coke, is not considered in the calculation.

7. **Coking Quality.**—(Not included in committee's report). The condition of the residue left in the crucible after the volatile matter has been expelled is a good indication of the coking qualities of a coal, and the latter may usually be reported as "coking" or "non-coking" accordingly. A better test, however, is to place a quantity of the coal in the shape of small fragments in a clay crucible, cover the latter and expose to a strong heat in a muffle. Be careful not to fill the crucible too full, or the mass may swell up and displace the cover. When all volatile matter has apparently been expelled and the crucible is at a bright red heat, remove from the muffle and allow to cool with the cover on. When cold, examine the residue, and from its fused or unfused condition, its porosity or density, etc., decide as to the quality of the coke. Of course this test is unnecessary with coals, such as

lignites, that give only a loose non-coherent residue in the platinum crucible after expelling the volatile matter.

8. Sulphur.—This is determined by Eschka's method as follows: Weigh 1 gram of the finely powdered coal into a platinum dish of 75- to 100-cc. capacity. Add 1.5 grams of an intimate mixture of 1 part dry sodium carbonate and 2 parts magnesium oxide. The magnesium oxide should be of a light and porous nature, not compact and heavy. Mix the coal and other constituents in the dish very thoroughly with a platinum spatula or glass rod. Now, holding the Bunsen burner in the hand at first, heat the dish very cautiously and raise the temperature very slowly, especially with soft coals. When the strong glowing has ceased, increase the heat gradually, placing the burner under the dish, until in about fifteen minutes the bottom of the dish is at a low red heat.*

Stir the mixture occasionally with a platinum rod and when the carbon is completely burned allow to cool and transfer the residue to a beaker. Rinse out the dish into the beaker with about 50 cc. of water, add 15 cc. of saturated bromine water and boil the mixture for five minutes. Remove from the heat, allow the insoluble matter to settle and decant the solution through a filter. Treat the residue twice with 30 cc. of water, bringing it to a boil each time, allowing to settle and decanting through the filter. Finally, transfer the residue to the filter and wash until the filtrate gives only a slight opalescence with nitric acid and silver nitrate. Add to the filtrate, which should have a volume of about 200 cc., 1.5 cc. of strong hydrochloric acid and boil the solution until the bromine is expelled. Now add to the boiling liquid 10 cc. of a 10 per cent solution of barium chloride. This should be added drop by drop, especially at first, with constant stirring. Allow to stand on a hot plate or over a low flame until the solution is perfectly clear, and then filter off the barium sulphate, washing with hot water until free from chlorides. Transfer the filter and moist precipitate to a weighed platinum crucible and heat with a low flame until the paper is burned. Finally heat to redness, cool in a desiccator and weigh the $BaSO_4$. The weight of the latter, multiplied by 0.1373 will give the weight of the sulphur, from which the percentage may be calculated.

To insure accuracy a blank determination should be made, using

* To avoid possible absorption of sulphur from the illuminating gas, it is advisable to place the dish in a hole cut in a piece of asbestos board.

all the reagents in the same quantities and carrying out the entire process in exactly the same manner as with the coal. Subtract the weight of any barium sulphate found from that obtained in the coal test and calculate the true percentage of sulphur in the coal from the remainder.

If the coal contains much pyrite or calcium sulphate, some sulphur may still remain with the residue of magnesium oxide and ash. Dissolve this residue in hydrochloric acid in slight excess, dilute sufficiently, heat to boiling and precipitate as above with barium chloride. Filter off any barium sulphate obtained, ignite, and weigh as before, and add the weight to that of the main portion. The experiments of Geo. Steiger, under the direction of Dr. Hillebrand, demonstrate the necessity of always examining this residue; nine samples of coal showing from 0.032 to 0.114 per cent additional sulphur, where the total sulphur ran from 0.625 to 4.561 per cent.

9. Error in Determining Volatile Combustible Matter.—Mead and Attix * call attention to the fact that while the above described method of heating over a Bunsen burner may be sufficient for soft coals it is quite inadequate for coke or anthracite, which require the heat of a blast-lamp to drive off all the volatile combustible matter. They further show that during this heating there is a considerable loss by oxidation. With coke and anthracite they therefore proceed as follows: Heat in an atmosphere of nitrogen, using a Shimer crucible,† first over a Bunsen burner for several minutes and then over a blast for fifteen minutes. As an alternative method, giving nearly the same results, omit the atmosphere of nitrogen but make two similar heatings and weighings, using an ordinary covered platinum crucible. The loss in a series of several consecutive heatings after the first is shown to be practically a constant, and is due entirely to oxidation. Therefore, deduct the loss sustained in the second heating from the loss in the first to obtain the loss due only to volatile combustible matter.

This method is undoubtedly much more satisfactory for coke and anthracite than the one given above, but as the results in any case are intended to be only comparative, it is perhaps not advisable to adopt it for ordinary work until there is some general agreement in the matter.

10. Phosphorus.—Weigh 5 grams of the coarsely crushed coal or coke (2) into a platinum dish and burn completely to ash, preferably in

* Jour. Am. Chem. Soc., XXI, 1137. † Jour. Am. Chem. Soc., XXI, 557.

a muffle. Transfer the residue to a beaker and digest with hydrochloric acid for some time to dissolve the phosphorus compounds, then filter into an 8-oz. beaker, washing with water, and evaporate the filtrate to dryness on a sand-bath or hot plate. Add to the residue in the beaker 25 cc. of strong nitric acid, cover the beaker and boil to about 12 cc. Now dilute with 12 cc. of water and filter, washing with water. Receive the filtrate in a 6-oz. flask. The total volume should not exceed 50 cc. Heat to 40°–45° C., add 60 cc. of molybdate solution (see PHOSPHORUS, 7), previously filtered and heated to 40°–45° C., stopper the flask and shake for five minutes. Allow to stand in a warm place for fifteen minutes and then filter through a Gooch crucible that has been previously dried at 110° C. and weighed. Wash with a 2 per cent nitric acid solution till free from salts, and then twice with 95 per cent alcohol. Dry twenty minutes at 110° C. and weigh. The dried residue contains 1.63 per cent of phosphorus; therefore multiply the weight found by 0.0163 to obtain the weight of phosphorus in the amount of coal taken.

Always test the filtrate with more molybdate solution, omitting the washings.

11. Specific Gravity.—In the matter of specific gravity, either one of two things may be required:

1. The *true* specific gravity, or specific gravity of the particles
2. The *apparent* specific gravity, or specific gravity of the mass taken as a whole.

Proceed as follows:

Select a lump of convenient size, weighing, perhaps, from 10 to 20 grams, and weigh it. Call this weight a.

Place the piece in distilled water under a bell-jar and exhaust the air from the latter. Admit the air, carefully wipe off the surface of the coal, now saturated with water, and weigh again.

Call the increase in weight, or weight of the absorbed water, b.

Now suspend the wet coal by means of a fine horse-hair and weigh it immersed in water. Call this weight c.

Then,

$$\frac{a}{a-c} = \text{true specific gravity,}$$

and

$$\frac{a}{a-(c-b)} = \text{apparent specific gravity.}$$

12. **Heating Value of Coal.**—The heating value of a coal is usually expressed either in terms of British Thermal Units (abbreviated, B.t.u.), or in Calories (abbreviated to Cal.).

The British Thermal Unit is the heat required to raise the temperature of 1 lb. of pure water, at or near its temperature of maximum density, 39.1 F., through 1° F.

The Calorie is the heat necessary to raise the temperature of 1 kg. of water from 4° C. to 5° C.

1 B.t.u. is equivalent to 0.252 Calorie.

1 Calorie is equivalent to 3.968 B.t.u.

To reduce B.t.u. per pound to Calories per kilogram, multiply by 5/9.

To reduce Calories per kilogram to B.t.u. per pound, multiply by 9/5.

The heating value of a coal is most accurately determined by means of a coal calorimeter, and a fairly correct result may be obtained by calculation from an ultimate analysis. Descriptions of both these methods may be found by consulting the standard authorities, but are omitted here as beyond the present scope of this treatise.* Attempts have been made to calculate the heating value of a coal from the results of its proximate analysis, and the following formulas are given as sufficiently accurate for rough heat calculations.

13. **Formula of F. Haas** (West Virginia Geol. Survey).

B.t.u. per pound = 156.75 (100 − per cent ash − per cent sulphur − per cent moisture) + (40.50 × per cent sulphur).

Calories per kilogram = 87.1 (100 − per cent ash − per cent sulphur − per cent moisture) + (25.50 × per cent sulphur).

14. **Goutal's Formula.**†

$82C + aV$ = calories per kilogram.

C = Fixed Carbon, V = Volatile Constituents, a is a variable factor dependent upon the Volatile Constituents, V_1, of the pure (water- and ash-free) coal.

$$V_1 = \frac{V \times 100}{C + V}.$$

15. The following table gives the values of a corresponding to values of V_1 from 1 to 40.

* See Chemical Engineer, Vol. I, pp. 1–98, for a clearly written article.

† Jour. f. Gasbeleuchtung u. Wasserorgung, XLVIII, 1006.

V_1	a	V_1	a	V_1	a	V_1	a	V_1	a	V_1	a	V_1	a
1–5	150	10	130	16	115	21	108	26	102	31	97	36	91
5	145	11	127	17	113	22	107	27	101	32	97	37	88
6	142	12	124	18	112	23	105	28	100	33	96	38	85
7	139	13	122	19	110	24	104	29	99	34	95	39	82
8	136	14	120	20	109	25	103	30	98	35	94	40	80
9	133	15	117										

16. As an example of how the results obtained by the above formulas compare with that of the bomb calorimeter, the following instance is given:

Proximate Analysis of Coal

Moisture	1.460
Volatile	10.880
Fixed carbon	81.535
Ash	6.125
	100.000
Sulphur	0.807

Calories per kilogram determined by calorimeter, 7778. by Haas's formula:

$$87.1\ (100-6.125-0.807-1.46)+(22.5\times 0.807)=7909 \text{ cal per kilo.}$$

By Goutal's formula:

$$V_1=\frac{10.88\times 100}{81.535+10.88=11.78}.$$

From the table we find that with V_1 equal to 11.78, $a=124.7$ Then,

$$82\ (81.535)+124.7\ (10.88)=8068 \text{ Cal. per kilo.}$$

CHAPTER XXXIV

TESTING CRUDE PETROLEUM

OWING to frequent discoveries of petroleum in new districts, the technical chemist is liable to be required to test and compare samples with a view to determining their commercial value. The following tests will usually suffice:

1. **Preliminary Note.**—The sample as received is likely to contain water, either because the original flow was mixed with water, or because the containing vessel was rinsed out with water and not subsequently dried. Therefore, allow the sample to stand for some time and settle out as much as possible before beginning the tests.

2. **Specific Gravity.**—This may be taken with the hydrometer if there is a sufficient quantity of the oil at hand. Fill the hydrometer jar about four-fifths full and introduce the hydrometer carefully so as not to smear the stem with oil above the point to which it would naturally sink. The hydrometer to employ is the "Standard Baumé Hydrometer for Coal Oil." Hold a piece of white paper back of the jar and note the point where the lower portion of the meniscus touches the scale. Also take the temperature of the oil and subtract 1° Baumé from the hydrometer reading for every increase of 10° F., or 5.5° C., above 60° F., or 15.5° C. The specific gravity may be found by comparing the hydrometer reading with a table (see p. 329), or by the formula $\frac{144.3}{134.3+B°}$. "B°" is the reading Baumé.

If the quantity of oil is too small for filling a hydrometer jar the specific gravity may be taken with a 10- or 25-cc. picnometer. The picnometer should be tested with water at 15.5° C. and then with the oil at the same temperature. The weight of the oil divided by the weight of the same volume of water, both at 15.5° C., will give the specific gravity at this temperature.

3. **Distillation Test, Engler's Method.**—Arrange a fractional distillation-flask with a side tube and Liebig condenser as in the figure.

The apparatus should be approximately of the dimensions shown. If possible, have the side tube long enough to permit of bending the outer end downward so as to fit into the vertical condenser. When this cannot be done without bringing the condenser and receiver too near the flame, use a properly bent glass tube as an extension. The joints may be cork, or strips of cotton cloth moistened with glycerin wrapped around and wound tightly with small string. Rubber will not answer so well, as it is acted upon by the hot vapors and may swell up or split. A Bunsen burner or alcohol lamp may be used for heating. A piece of wire gauze may be placed under the flask at first and afterward removed and the naked flame employed as a higher temperature is required. The flame should be screened to protect it from draughts.

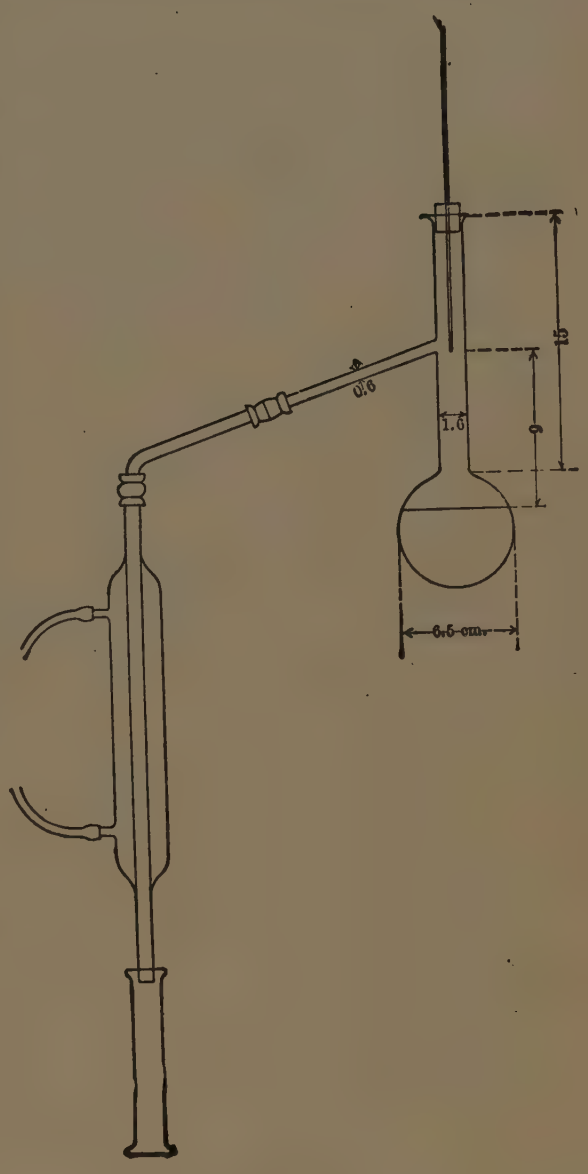

FIG. 21.

4. By means of a graduated pipette, place 100 cc. of the oil in the flask and then arrange a thermometer, graduated to 400° C., inserted through a cork in the top of the flask, so that the top of the bulb is about opposite the junction of the side tube and neck of the flask. Heat the oil so that it distills as nearly as possible at the rate of 2 to 2.5 cc. per minute. As the temperature rises above 100° C. be watchful for water in the oil. Water is apt to cause sudden violent bumps when it collects under the oil. It also evaporates, and a portion condenses in a drop on the thermometer bulb. When this drop falls back into the hot oil it is liable to cause a small explosion and perhaps spoil the analysis. It is best to heat very cautiously at first, and, if water appears on the bulb, to remove the thermometer and absorb

it with filter-paper.* Oils with but little naphtha are apt to give the most trouble in this respect, as they may become very hot and dangerous before the thermometer in the neck shows much rise, and if a drop of water then falls back a violent burst of steam is the result. Continue the heating until the thermometer indicates a temperature of 150° C. Collect the distillate in a 50-cc. cylindrical graduate. When a temperature of 150° is reached, remove the lamp a moment so that the temperature will drop back 20°, then replace it and again heat to 150°. Repeat these operations until no appreciable additional distillate is thus obtained. Read the number of cubic centimeters in the graduate, quickly pour out the oil and replace the graduate again. Now increase the heat so that the thermometer gradually rises to 200° and then repeat the cooling and heating as before. Measure the fraction thus obtained and then increase the heat similarly to 250° and 300°,† and then above 300°, until nothing but coke remains in the flask. The distillate up to 150° is called naphtha. The next three portions are illuminating oils, the fractions obtained showing the proportions of the different grades. The distillate coming off above 300° is called lubricating oil, and what is finally left in the flask constitutes the residuum and coke. The distillation is usually carried as far as possible.

EXAMPLE SHOWING TABULATION OF RESULTS

Specific gravity of the crude oil at 60° Fahr., 0.841

Temperature of Distillation.	Per Cent. of Product.		Nature of Product.
Below 150° C.	28.5		Naphtha
From 150° to 200°	12.5	Total 66.5	Illuminating-oils
" 200° " 250°	13.0		
" 250° " 300°	41.0		
Above 300°	2.0		Lubricating-oil
Residue	3.0		Coke
	100.0		

* A safer plan is to lower the thermometer so that the bulb is immersed in the liquid, until a temperature of, say 120° C. is attained, occasionally agitating the flask until all water is expelled. Then raise the thermometer to its proper place and proceed as described.

† I have found it best, at this point, to stop the flow of cold water and cautiously heat that standing in the condenser, with a soft flame, so as to prevent subsequent products from thickening or solidifying in the tube.

DISTILLATION OF OIL SHALE *

The following is the ordinary method employed at the Colorado School of Mines for the preliminary testing of oil shales, oil being the primary consideration. The conditions of the distillation are easy to maintain and duplicates check closely. While the results may be regarded as only approximately correct, they nevertheless serve as a reliable basis of comparison between different shales and thus satisfactorily answer the purpose for which the apparatus was designed.

Referring to the diagram, the retort *A* is constructed from a piece

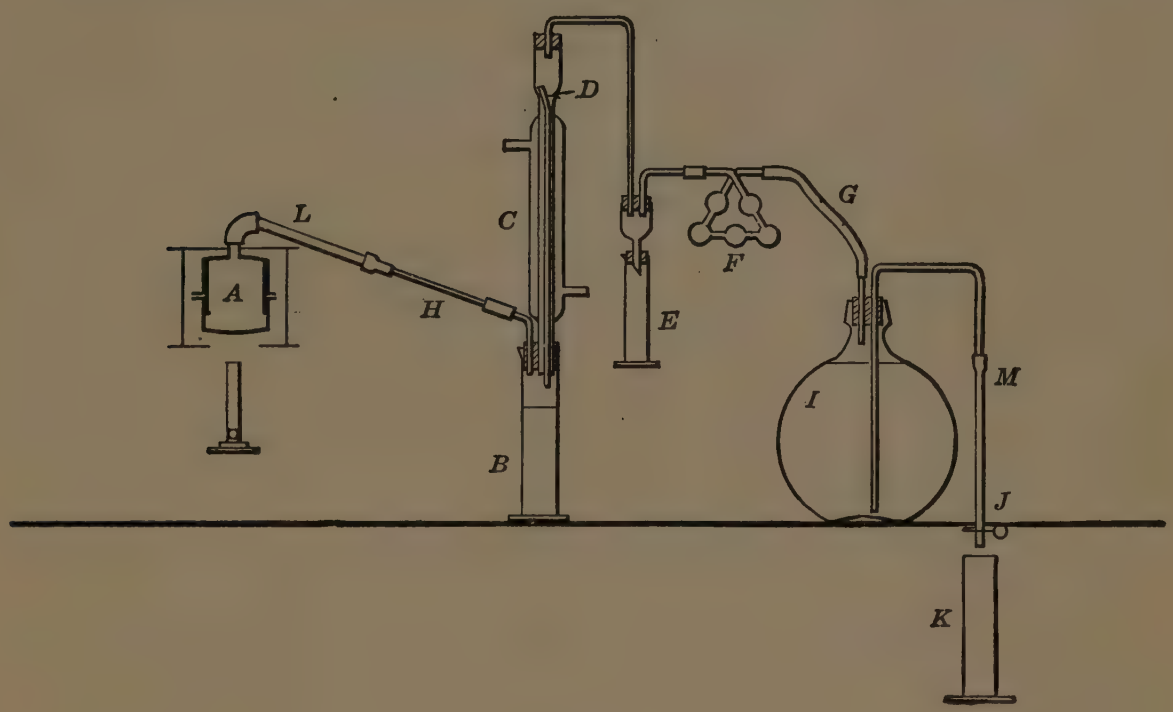

FIG. 22.

of ordinary 3-in. iron pipe, 2 in. long and threaded at both ends. Both ends are capped, but with this difference: the lower cap is tightly screwed on the usual threads, while the threads on the upper end of the pipe are continued downward sufficiently to allow the cap to be screwed completely down until the top meets the pipe. This cap should screw easily on and off by hand. The distance between the edges of the two

* A. H. Low, School of Mines Quarterly, April, 1921.

caps, when in place, should be about $\frac{1}{8}$ in. The capacity of the retort is gauged to easily hold 241 grams of most shales when crushed to $\frac{1}{4}$-in. size. A short tube and elbow are fitted in the upper cap, from which the $\frac{1}{4}$-in. gas pipe *L* runs downward for about 15 in. at an angle of about 20°. The gas pipe is joined by a rubber connector to the glass tube *H*, about 11 in. long. This tube, in turn, similarly connects with a tube running through a closely fitting rubber stopper into the graduated cylinder *B*. For ordinary shales this is a 100-cc. graduate. The condenser *C* has a small tin or lead pipe *D* passing loosely through its entire length. This pipe is about $\frac{1}{4}$ in. external diameter and is open at both ends. The upper end is bent slightly to act as a support. *E* is a 10-cc. graduate, fitted with a rubber stopper through which passes the stem of a small Gooch funnel. The exit tube from this funnel connects with the absorption bulbs *F*, and they in turn connect by the rubber tube *G* with the carboy *I*, which is nearly filled with water. The tube *M* runs from the bottom of the carboy as shown, and has a piece of rubber tubing attached to the outer end. The entire tube is filled with water at the outset and closed at the end by the pinch cock *J*. *K* is a 1000-cc. graduate. The retort is entirely surrounded by a shield of thin asbestos board. The necessary slit in the piece covering the top affords sufficient draft. The bottom piece, which rests on a large ring of a ring stand and supports the whole, has a large hole in the center for the burner flame. The heat is supplied by one or more Bunsen or other burners, sufficiently powerful to eventually heat the retort to a dull red. The retort may be supported by a large ring-stand with a suitable clamp attached near the retort in the pipe *L*.

Have the apparatus, with the exception of the retort, assembled as shown, the carboy being nearly filled with cold water, the siphon tube full and the pinch cock closed. Have about 20 cc. of about one-fifth normal sulphuric acid in the absorption bulbs, slightly tinted with methyl orange to be certain that the acid is not entirely neutralized during the distillation. Cold water should flow through the condenser from start to finish. The retort with its attached pipe *L* is now ready for charging. Have the dry shale crushed to about $\frac{1}{4}$ in. size. Weigh 241 grams into the retort and screw down the cap as far as it will go, but not tightly, or it may be impossible to unscrew it by hand after the distillation. Fill the narrow space between the two caps with "Engineer's No. 1, Smooth On" cement, or other suitable lute.

Smooth On cement will soon set and there is little danger of leaking, even though the upper cap be not screwed down firmly. Now put the retort and asbestos shields in place and then open the pinch cock *J* and see that there is no leakage anywhere. The rubber tube to which the pinch cock is attached is shown hanging straight downward in the diagram. At the outset the lower end should be raised on a suitable support, to considerably lessen the pull of the siphon. As the distillation proceeds the end should be gradually lowered. The entire overflow from the carboy is caught and measured. When all is ready, begin heating the retort with a single burner turned on full. Continue this until the oil begins to come over. Now watch the operation closely. As long as no yellowish fumes appear in the cylinder *B*, all is well. Do not mistake steam for these fumes, however. As the distillation proceeds, the heat may be gradually increased, and a second or third burner may be added, but whenever yellow fumes begin to appear the heat must be at once diminished until they cease. The yellow fumes are the warning signal of overheating. When near the end, however, a strong heat is necessary to obtain the last portion of oil, and yellow fumes are then usually unavoidable. The operation is ended when no more gas bubbles through the absorption bulbs. The lower half of the retort should be of a dull-red heat. Oil usually stops coming over some time before the gas ceases.

When the operation is finally finished, close the pinch cock *J* and immediately separate the tubes *L* and *H*. Read the cubic centimeters of oil and also of water in the cylinder *B*, and the oil in the small graduate *E*. The amount in the latter should be very small, even negligible. Each cubic centimeter of oil or of water represents 1 gal. per ton of shale, when 241 grams of shale are taken for the distillation. Now run a little hot water through the glass tube *H* into the cylinder, and also similarly through the condenser. This is to recover any ammonia compounds on the walls. Disconnect the cylinder *B* and transfer the contents to a separatory funnel. After the separation, run the water into a beaker and wash the oil twice with warm water without shaking, running the wash water into the same beaker. Add the contents of the absorption bulbs and determine the ammonia in the total by the Kjeldahl method, finally titrating with N/5 normal H_2SO_4. When 241 grams of shale are used for the distillation, each cubic centimeter of N/5 H_2SO_4 required is equivalent to 0.10954 lb.

of ammonia sulphate $(NH_4)_2SO_4$ per ton of shale. The volume of water that has overflowed from the carboy is equal to the volume of permanent gases evolved from the shale. This volume in cubic centimeters multiplied by 0.1329 equals the yield of permanent gases in cubic feet per ton of shale, when 241 grams have been taken for the distillation.

When the distillation is made for oil only, the absorption bulbs and carboy are, of course, omitted and the operation is ended when the oil ceases to come over.

Among the advantages of the above retort are its freedom from leakage and the ease with which it can be dismantled. When cold, the cement can be quickly loosened with a hammer and the top unscrewed by hand. It is constructed from materials easily obtained, the iron pipe and caps being of standard sizes.

The tin or lead pipe running through the condenser adds greatly to the condensing effect, the arrangement catching much of the mist that would ordinarily escape. Some of this mist inevitably escapes the condenser, most of which, however, is recovered as oil in *E*. As the condenser is placed at the exit of the cylinder *B*, instead of between the retort and cylinder, it does not become clogged with heavy products requiring subsequent warming to remove them. The pipe *L* remains hot enough to prevent accumulation of these products, and if any are seen in the glass tube *H* they are easily removed by the short application of a flame.

MISCELLANEOUS

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DETERMINATION OF ANTIMONY AND TIN IN BABBITT TYPE METAL AND OTHER ALLOYS

The following process,* found generally applicable to alloys and to the sulphides of antimony and tin, either in the solid state or in proper solution, claims nothing in particular as original, except the direct determination of the antimony and tin in one portion of the alloy without separating the other ingredients, and the titration of antimony and tin when both are present in solution. The direct titration in an alloy without separation of the other ingredients may not be applicable in all cases, but it is in most cases, and where it is not the sulphide separation mentioned below is made use of, and the sulphides treated in almost the same way as the original alloy. If other metals, beside tin and antimony, are to be determined, Rossing's method given below gives a good, quick separation, but the antimony and tin are determined by direct titration, if possible, in another portion of the alloy.

Where only antimony and tin are sought, the alloy may be decomposed by nitric acid, by sulphuric acid, or by a mixture of sulphuric acid and potassium sulphate. Where possible, sulphuric acid alone is used. If nitric acid is first used, it must subsequently be expelled by boiling with sulphuric acid, and after the nitric acid is expelled, some tartaric acid and some potassium sulphate must be added, and the melt heated till all carbon has been oxidized. This leaves the antimony and tin in the proper state for the titrations.

The two standard solutions required are an N/10 potassium permanganate, and an N/10 iodine solution. For antimony determination, the permanganate solution should be standardized by C. P. antimony or tartar emetic (anhydrous) of the proper composition. If properly done, these standards will agree, and both will agree with a standardization made with oxalic acid in the regular way. Always standardize with antimony or its compounds by heating with sulphuric acid, diluting and adding the same amount of hydrochloric acid as is used with the alloy. In this way correct results are insured. The iodine solution is compared with a solution of sodium thiosulphate of known value.

From 0.5 gram to 1 gram of the finely divided alloy is taken.

* Method of W. H. Low, Jour. Am. Chem. Soc., XXIX, 66.

As the method is in general the same, the standardization of the permanganate will be described together with the subsequent titration of the tin.

Place 0.1202 gram of finely powdered C.P. antimony (=0.3234 gram tartar emetic) and 0.1190 gram of tin in a 450-cc. Jena glass Erlenmeyer flask and add about 10 cc. of strong sulphuric acid (free from chlorine compounds); 3–4 grams of potassium sulphate are sometimes used and can be added here. Heat till the metals are all in solution (or the alloy thoroughly decomposed) and all separated sulphur has been boiled out of the flask. All sulphurous acid will also be expelled by this time. Do not drive off all free sulphuric acid, but have enough left to keep the melt from getting hard on cooling—say about 7–10 cm. These operations take only a few minutes. Cool and add 50 cc. of water and 10 cc. of strong hydrochloric acid and heat to get all possible in solution. Large quantities of lead sulphate, even, will dissolve, and the solution will become clear. However, the object is to get the antimony and tin in solution, and this is all that is necessary. With the quantity of antimony taken, no tartaric acid is necessary, but with larger quantities a few grams of tartaric acid must be added. Tartaric acid has no effect on either titration. Some stannic compound with sulphuric acid may go into solution with some difficulty, but no attention need be paid to it here, as it will dissolve when we get through with the antimony, if not before. Cool the solution and add about 110 cc. more of water and 25–30 cc. more of strong hydrochloric acid. (With small amounts of Sb, as in solder, a total of 20 cc. strong HCl in total volume of 200 cc. appears enough.) Thoroughly cool this mixture and proceed to titrate with permanganate. Add the latter till the last drop colors the whole solution pink. The end-point is sharp, but the color may not remain long, owing to the large quantity of hydrochloric acid present. If less hydrochloric acid were present, say 10 cc. in the total volume of 200 cc., the end-point would be sharp, but would apparently occur at about 19.60–19.70 cc. instead of 20.00 cc., as it should. The true end-point under these circumstances is troublesome to find. But even an incorrect end-point may give good results, if the solution has been standardized in exactly the same way. The determination of the antimony or standardization of the permanganate is now finished and the tin is the next consideration. The titrated solution contains antimonic chloride and stannic chloride, besides other things of no

particular moment. Pour this solution into a 500-cc. round-bottom flask and rinse out the Erlenmeyer flask with about 50 cc. of strong hydrochloric acid and add washings to main solution. The main solution should be at least one-fifth by volume of strong hydrochloric acid (the regular strong C.P. acid). Add about 1 gram of finely powdered C.P. antimony * and place on the steam-bath for about fifteen minutes, shaking once in a while. Next remove from the bath and connect with an apparatus capable of giving a rapid current of carbon dioxide. The connection is made by means of a cork carrying two tubes. The first dips below the surface of the solution in the flask and the second or outlet tube is bent downward and the end dips slightly below the surface of some water or mercury. This allows any tendency to back pressure to be instantly detected. While passing a rapid stream of gas, heat the contents of the flask to boiling, using a naked flame, but taking care to heat the sides of the flask and avoid directly heating the bottom. This is because the antimony lies on the bottom and the flask might be cracked by unequal heating in contact with solution. Boil 2–3 minutes after the liquid commences to boil. Cool quickly by surrounding the flask with cold water and take care that the current of carbon dioxide is strong enough to prevent back pressure due to sudden condensation. When cold, loosen the cork somewhat and introduce 5 cc. of good starch solution, and then withdraw the flask gently so as not to allow air to enter by forming currents. Cork quickly and take to the burette. Introduce the spit of the burette far down into the neck of the flask and, rotating the latter gently, run in or drop in N/10 iodine solution. Towards the end the starch blue will appear and remain mostly in the middle portion of the solution, requiring stronger agitation to mix with the rest of the solution. This causes the metallic antimony in the bottom of the flask to become stirred up and slightly obscure any slight blue tint. For this reason the titration is continued till the last drop gives a strong blue to the whole solution, and then we deduct about 0.05 cc. from the burette reading. Do not fear that the end-point will not be recognized within one drop or less. It is unmistakable with good starch solution, and no doubtful ending should be taken. With correct solutions, etc., the titration should have taken just 20.00 cc. Mixtures of C.P. antimony and C.P. tin (allowing for 0.10 per cent impurities found to be present) give exact results. No trouble has been

* Ibbotson and Brearley, Analyst, 1902, 25.

found in titrating tin correctly with iodine. Objections to this method may be founded from accepting C.P. tin as actually nothing but tin, while most of it contains impurity.

To test tin or antimony for impurity, a quick method, of considerable accuracy, is to take about 0.5 gram in a porcelain boat, place in a combustion tube and pass a slow current of dry chlorine or dry hydrochloric acid gas. The tin or antimony is quickly volatilized and lead, copper, iron, etc., remain mostly in the boat. Displacing the chlorine with carbon dioxide and then heating in a current of hydrogen reduces the chlorides left in the boat to metal, and their weight can be deducted from the original metal, or the percentage determined. This is not strictly accurate, as on first heating in hydrogen there is a slight volatilization of some of the chlorides.

In the case of an alloy, a good qualitative analysis should always be made, unless the approximate composition is known. If there are no interfering metals, the alloy is decomposed and the antimony and tin titrated, as shown above, without removing the lead sulphate, copper sulphate, etc. Lead in large amount does not interfere. Theoretically, any amount of copper should not interfere, and practically small amounts are known to cause no trouble, while large amounts have not been present in the tests made. Should the alloy contain iron in any quantity, there might be some danger of ferrous sulphate being left after boiling with sulphuric acid. This difficulty is overcome by decomposing the alloy with nitric acid, as usual, boiling off most of the nitric acid, adding about 10 cc. of sulphuric acid and 3–4 grams potassium sulphate, boiling to complete expulsion of the nitric acid, and then adding a little tartaric acid or other organic matter, and after the carbonization, continuing the boiling till all organic matter has been destroyed. This will always leave the antimony and tin in the "ous" and "ic" states, respectively.* From this point, the determination is carried on in the manner described above. Where the antimony and tin have been separated from the other metals by means of alkaline sulphides, the details of operation depend on whether the decomposition of the alloy was made with aqua regia or with sulphuric or nitric acid. It will be assumed that the alloy has been dissolved in aqua regia and the tin and antimony are in solution combined with alkaline sulphides. Add slight excess of sulphuric acid and heat gently to precipitate the sulphides of antimony

* A. H. Low, Jour. Am. Chem. Soc., XXVIII, 1715.

and tin. Filter, preferably through a 60 mm. Witt's plate and an S. & S. white ribbon filter No. 589, and wash the precipitate on the filter with dilute hydrogen sulphide water containing enough ammonium acetate to prevent stannic sulphide from giving a turbid or opalescent filtrate. After washing somewhat, test each succeeding 10–20 cc. of filtrate by boiling off the hydrogen sulphide, acidifying with nitric acid and adding three or four drops of silver nitrate solution. The last filtrate should be entirely free from chlorine, as shown by this test. With a Witt's plate of 60 mm. diameter, this is quickly accomplished. The residue on the filter and the filter itself may now be placed in a 450 cc. Jena glass Erlenmeyer flask, 3–4 grams potassium sulphate added and 10–20 cc. strong sulphuric acid, and the whole mass boiled till all organic matter has been destroyed and the antimony and tin are present as sulphates, while there are not over 10 cc. of free sulphuric acid left in the flask. As organic matter is not really necessary in this operation, and it takes some time to oxidize the filter paper, the precipitate on the filter can be handled differently, if some alkaline sulphide, free from chlorine compounds, is available. This desideratum will probably be found best in ammonium sulphides or poly-sulphides, as the best C.P. by alcohol caustic soda contains enough chloride to cause some loss of tin. The precipitate is washed from the filter into the flask with as small a quantity of water as possible. What remains on the filter is dissolved off with alkaline sulphide free from chlorine and the solution added to the flask. Enough alkaline sulphide is now added to the flask to dissolve the sulphides of antimony and tin on warming. When this is accomplished, acidify with sulphuric acid and then add about 10–15 cc. in excess and 3–4 grams potassium sulphate and boil down to sulphuric acid fumes and till all sulphur has been expelled and the antimony and tin remain only as sulphates. The final amount of free sulphuric acid left should not be over 10 cc. Tin tends to form a stannic sulphate, very insoluble in strong sulphuric acid, but subsequent heating and boiling in the presence of hydrochloric acid dissolves it. The boiling with strong sulphuric acid and destruction of organic matter is carried on easily and quickly over a naked flame of good heating power. The Jena glass Erlenmeyer flasks stand the operation very well, and none have cracked. The flask is generally held in the hand by means of a clamp (Chaddocks' clamp with rubber removed is very good) and rotated to insure even heating. In this way the sulphuric acid may be com-

pletely driven off, leaving a melt of acid potassium sulphate, and the flask will not break. If there is any doubt that the antimony does not exist in the "ous" condition, a little tartaric acid or other organic matter may be added and burned off by boiling. The antimony and tin now exist as sulphates and the procedure is the same as in the standardization of the permanganate.

This method for the sulphides of antimony and tin is in every way much more satisfactory than the gravimetric separation and determination, and takes little time.

Mixtures of C.P. antimony and tin (allowing for any impurities) give exact results. An alloy run through recently gave the following results. Qualitative analysis showed the metals indicated to be the only ones present, except in minute traces.

Lead	74.19	Alloy dissolved in aqua regia, alkaline sulphide separation, lead separated from copper as sulphate in presence of alcohol. Two determinations checked.
Antimony	15.44	Alloy boiled with sulphuric acid and antimony titrated direct, as in standardizing permanganate.
Tin	9.88	Determined in same solution, after the antimony.
Copper	0.44	Determined after the lead, driving off alcohol and determining by A. H. Low's iodide process. Check test.
Iron	trace	
	99.95	

If arsenic were present, it would interfere with the antimony titration or be counted as antimony. It may easily be removed.

It is often stated that the titration of tin with iodine gives slightly low results. Experience with the above method has given confidence that the results for tin are exact, if the conditions are observed. Tin may be lost somewhere in the process, but all that remains is surely indicated by the titration.

Method of A. Rossing for Separation of Sulphides.*—In this method the alloy is dissolved in a minimum of aqua regia, a little potassium chlorate being used to insure complete oxidation. After some dilution, a little tartaric acid is added, the solution almost exactly neutralized with sodium hydroxide solution and a sufficient quantity of colorless sodium hydrosulphide, NaSH, added to precip-

* Jour. Soc. Chem. Ind., 1902, 191.

itate copper, lead, etc., and to retain all the antimony and tin in solution. By using a gentle heat and with enough sodium sulphide, the antimony and tin will go into solution. Filter, washing the residue with hot dilute sodium sulphide solution. Test the final washings by acidifying them, to make sure of the removal of all the antimony and tin from the residue.

SULPHUR DIOXIDE METHOD FOR DETERMINING COPPER MINERALS IN PARTLY OXIDIZED ORES*

A survey of the status of present laboratory practice brought out the need of a correct and rapid method for the selective determination of the quantity of copper in the sulphide form, on the one hand, and of that in the form of combined oxides, carbonates, silicates, and native or metallic copper, on the other hand, in partly oxidized ores and in mill products from these ores. Such a method is necessary for control determination on flotation mills treating sulphide ores, and also on lixiviation works using either acids or alkalies as the active solvent for the copper in oxidized and in silicate form. For convenience, such copper is termed " oxidized copper."

Procedure.—Place 2 grams of pulp, ground to a fineness of 100 to 150 mesh, in a bottle, and 100 cc. of a 3 per cent solution of sulphur dioxide. Seal the bottle and agitate by rolling for one-half to two hours. Filter; wash the residue with sulphur dioxide solution; add the washings to the filtrate, which will contain in solution all oxides, carbonates and silicates of copper, and all metallic copper. Add 5 to 10 cc. of nitric acid and boil down to 20 cc. Dilute with distilled water to 150 cc. and determine the copper by the electrolytic method in the usual way.

The residue from the filtration contains the unaltered and undissolved copper sulphides. In the experimental work the copper present as sulphide was separately determined, in order to check the determination of oxidized copper. Ordinarily this step would not be necessary. In analyses of the low-grade porphyry copper ores of the Southwest, the sulphides may be readily decomposed and all the copper dissolved by proceeding as follows: To the residue, add 5 cc. of

* Barneveld and Leaver. U. S. Bureau of Mines, Technical paper, 198.

sulphuric acid and 10 cc. of nitric acid and boil until dense white fumes appear. Add 5 cc. of nitric acid and dilute with distilled water to 150 cc. Determine the copper by the electrolytic method. This method of determining copper in the residue is not suited for heavy sulphide ores containing interfering bases, and for such ores standard methods should be used.

Preparation of Solution.—Although sulphur dioxide solution (sulphurous acid) may be readily purchased, it is decidedly unstable; hence the solution should be prepared in the laboratory as needed. Small quantities are easily made by adding moderately strong sulphuric acid to scrap copper tinned on one side; the resulting sulphur dioxide gas is absorbed in water. For continuous work it is better to purchase liquid sulphur dioxide in steel cylinders and drums, which are obtainable in sizes ranging from 6-lb. to 200-lb. capacity. In the first experiments at the Tucson station the sulphur dioxide gas was introduced directly into the bottle containing the water and pulp. Much loss of gas resulted and the procedure was otherwise unsatisfactory.

Later the simple apparatus shown in Fig. 23 was evolved. A vertical absorption tower *a*, 42 in. long, made of $\frac{3}{4}$-in. to 1-in. glass tubing and filled with broken hard-burned fire clay, is set between two glass bottles *b* and *d*, of 3 to 5 gals. capacity, the bottle *b* being placed about 5 ft. above the other bottle. This tower is open at the top and sealed at the bottom with a plug of sealing wax *e*, through which two small glass tubes extend. The upper bottle *b* contains distilled water, which is siphoned into the upper end of the absorption tower, the flow being regulated by a stopcock *f*. A cylinder *c* (capacity 6 to 50 lbs.), containing liquid sulphur dioxide, is connected to one of the glass tubes extending into the absorption tower. On opening the valve of this cylinder the liquid sulphur dioxide issuing from the valve is gasified by the reduction in pressure and passes into the tower, where it is absorbed by the water from bottle *b*, converted into sulphur dioxide solution of the desired strength and caught in the stock bottle *d*.

This apparatus gives entire satisfaction. With little attention, a 3 per cent solution of sulphur dioxide may be produced at the rate of 3 liters per hour. The cylinder containing liquid sulphur dioxide indicated in the sketch may be replaced with an SO_2 gas generator.

Strength of Solution and Time of Contact.—Considerable variation as regards strength of solution and time of contact will be necessary in treating different ores from different localities. In general, for porphyry copper ores a solution containing 3 per cent sulphur dioxide

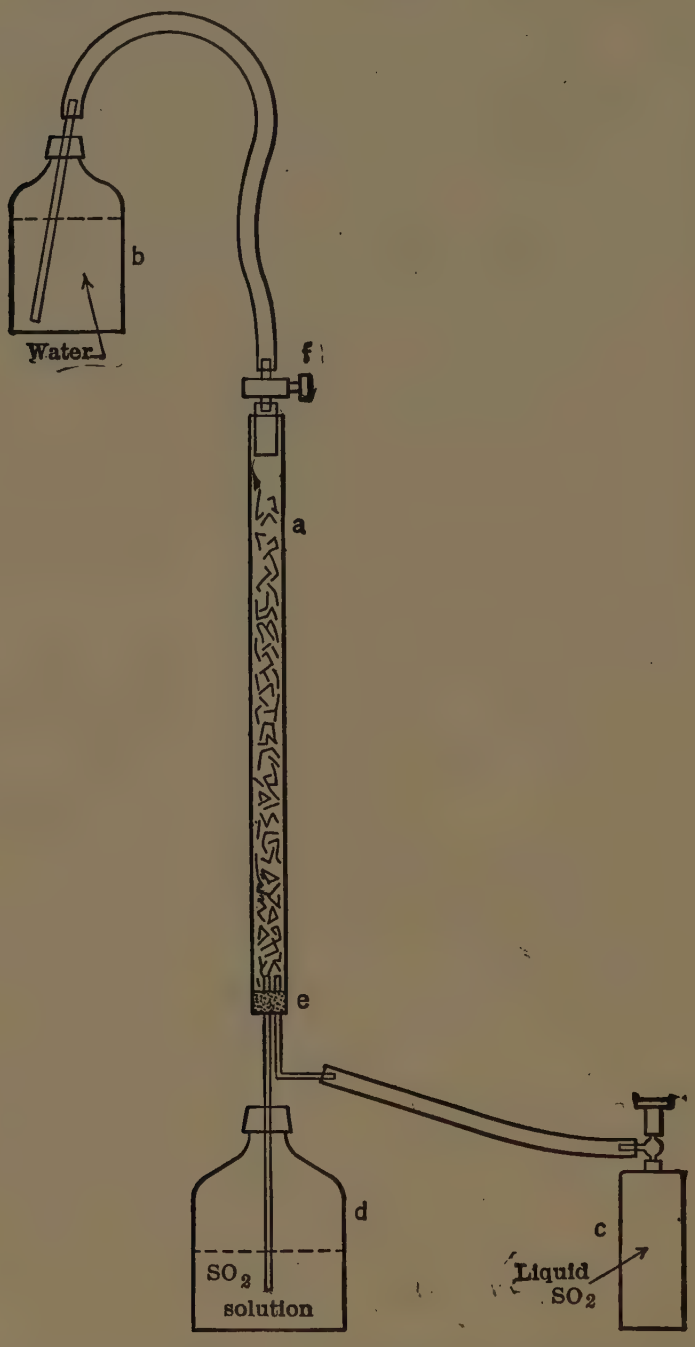

FIG. 23.—Apparatus for Preparation of Sulphur Dioxide Solution: *a*, absorption tower; *b*, distilled water bottle; *c*, container for liquid sulphur dioxide; *d*, bottle for sulphur dioxide solution; *e*, plug of sealing wax.

should be used. With some ores much weaker solutions, containing as low as 0.75 per cent sulphur dioxide, will do the work. Merely introducing the pulp into the solution, shaking the bottle for a few

minutes, and letting it stand, will not dissolve the copper; constant agitation is essential. For a small number of tests a bottle-agitating machine will give satisfactory results. For analytical work, where large numbers of samples are run, as in a mine laboratory, a bottle-rolling machine will be found more satisfactory, not only for this purpose, but for all solutions requiring constant agitation. The time of contact necessary to completely dissolve the oxidized copper minerals was found to vary from one-half to two hours. Most of the ores and products tested gave complete recovery in half an hour, and the most refractory ores yielded in less than two hours.

Testing Strength of Solution.—To determine the strength of the sulphur dioxide solution, the following adaptation of a well-known reaction is recommended. It is based on the fact that introducing either weak or concentrated sulphurous acid into a solution of iodine will result in the complete oxidation of the sulphur dioxide.

Prepare an iodine solution by dissolving 16.8 grams of potassium iodide in distilled water, adding 8.4 grams of pure resublimed iodine, and shaking until the iodine is completely dissolved. The more concentrated the potassium iodide solution, the more readily will the iodine dissolve. Bring the solution to proper strength by adding enough distilled water to make a volume of 1 liter. Then standardize the solution by the thiosulphate method, using starch indicator.

The determination is made as follows: To a measured quantity of standard iodine solution add slowly, with constant stirring, the proper volume of sulphur dioxide solution. So regulate the volume of iodine solution used that the mixture always contains a decided excess of iodine over the quantity required to oxidize the sulphur dioxide being added. An excess of sulphur dioxide causes the solution to clear and to lose its dark red color. If an excess of sulphur dioxide is added, the determination is spoiled, and the test should be repeated with fresh sulphur dioxide solution and a larger quantity of iodine solution. Thus, there is a relation between the strength and quantity of sulphur dioxide solution and the quantity of standard iodine solution. In general, when the solution to be standardized varies in strength from 1 to 3 per cent sulphur dioxide, add 1 cc. of this solution to 20 cc. of standard iodine solution. When the sulphur dioxide solution is appreciable below 1 per cent in strength add a larger quantity of it. The mixture is then titrated by the thiosulphate method to determine the quantity of iodine remaining in the mixture. The difference

between this quantity and the total quantity of iodine represents the iodine used in oxidizing the sulphur dioxide. The strength of the sulphur dioxide solution may then be calculated according to the formula:

$$SO_2+H_2O+2I=2HI+SO_3.$$

Metallic iron, from the grinding, etc., in amount up to 2 per cent is without influence on the results. The amount found in finely ground ores is usually less than 1 per cent. An essential requirement is the continued presence of a strong excess of SO_2, which readily dissolves the metallic iron. In order to insure this excess, the SO_2 must be introduced in the form of sulphur dioxide solution. If SO_2 is introduced in the form of a gas, unstable conditions arise from the unequal distribution of the gas; then the presence of metallic iron, in quantities less than 2 per cent may cause the precipitation of copper in the form of cement copper cupro-cupric sulphites, and probably also as complex sulphides, which are not redissolved.

DETERMINATION OF ARSENIC IN CRUDE SULPHUR

Weigh 10 grams (or more, if considered necessary) of the dry crude sulphur into a tall, narrow beaker of about 200 cc. capacity. Add sufficient carbon disulphide to dissolve practically all the sulphur, perhaps 30 to 50 cc. A small amount of the sulphur may exist as a modification insoluble in carbon disulphide. The failure of this to dissolve is usually immaterial. Add 50 cc. of water containing about 7 cc. of strong ammonia. Place the beaker in hot water, repeatedly renewed, until all the carbon disulphide has boiled away. Most of the sulphur precipitates. A little remains in solution as ammonium sulphide, and this solution contains all the arsenic. Filter, washing with warm water. Receive the filtrate in an 8-oz. flask. Add 1 gram of sodium carbonate and boil until all the ammonia is expelled. Now add 3 grams of anhydrous sodium sulphate and 5 cc. of strong sulphuric acid. Boil until all the free acid is expelled and the contents of the flask reduced to a melt. Cool with the flask inclined, to prevent the cake from cracking the bottom. Add 50 cc. of hot water and boil to dissolve the cake. Finish by the iodine method, as

described in ARSENIC, 1. Use an iodine solution of about one-fifth the usual strength. Report in parts per million. If As_2O_3 is required, $As \times 1.32 = As_2O_3$.

Run a blank test by placing in a flask 1 gram of sodium carbonate, 3 grams of sodium sulphate and 5 cc. of sulphuric acid, running the mixture down and finishing as above. Deduct the iodine required for the blank from that used in the analysis before making the calculation for arsenic.

Note.—I have found results obtained by the above method (which takes only one or two hours) to closely check those obtained by much more tedious and elaborate schemes.

DETERMINATION OF ARSENIC AND ANTIMONY.* DISTILLATION METHOD

Solutions:

Copper, Zinc Chloride.—To 1 lb. of C. P. stick zinc, add 500 cc. of water and then, gradually, 1200 cc. of C.P. hydrochloric acid. Boil the solution until it reaches a temperature of 108° C.

Dissolve 300 grams of C. P. cupric chloride in 1 liter of C. P. hydrochloric acid (sp. gr. 1.18) and mix this solution with the one made as above.

Standard Iodine Solution.—Dissolve 75 grams of potassium iodide in as little water as possible and use this as a solvent for 34 grams of pure iodine. Make up to 2 liters. One cubic centimeter of this solution will be approximately equivalent to 0.005 gram of arsenic.

To standardize: Weigh 300 mg. of pure arsenious oxide (As_2O_3) into an 8-oz. flask. Add 20 cc. of water and about 2 grams of sodium hydroxide. When the arsenic has dissolved, dilute to about 200 cc., add a drop or two of phenolphthalein solution as indicator and then make faintly acid with hydrochloric acid. Now add 2 grams of sodium acid carbonate and a little starch solution, then cool thoroughly and titrate with the standard iodine solution to a permanent blue tinge. Three hundred milligrams of As_2O_3 are equivalent to 0.2273 gram of As.

Divide this weight by the number of cubic centimeters of iodine solution used to obtain the value of 1 cc. in As.

* Communicated by Lewis B. Skinner, formerly Vice Pres. and Gen. Mgr., Western Chemical Mfg. Co.

Notes.—Be careful in acidifying with hydrochloric acid, as above, to add only a slight excess; otherwise the 2 grams of sodium acid carbonate prescribed may be insufficient to completely neutralize it, as required. Also, do not fail to cool thoroughly before titrating.

A blank should be run on the copper, zinc chloride solution, since the copper salt used may contain nitrogen compounds or arsenic. Distill the amount indicated for a regular determination, in the manner to be described, with 0.25 gram of C. P. copper, finally titrating as usual. Deduct the amount of iodine solution required from the amount used with unknowns.

Arsenic Determination.—In the case of heavy sulphides, low in arsenic, weigh 10 grams of the finely ground pulp into a 12-oz. flask and digest with 20 grams of potassium acid sulphate, one-half of an 11-cm. filter paper and 50 cc. of strong sulphuric acid. This method of attack is due to A. H. Low.

Bring the acid to a boil and fume it until the sulphur is expelled and the black color, due to carbon, disappears. Allow the melt to cool with the flask on its side, to avoid cracking. When cool, carefully add 100 cc. of water, then 25 cc. of hydrochloric acid and 2 or 3 grams of tartaric acid. Heat to just below boiling, or, better, a little cooler, until all anhydrous ferric sulphate has dissolved. If the solution is allowed to boil, arsenic is liable to be lost by volatilization. Filter, dilute the filtrate to about 300 cc. with hot water, and pass in hydrogen sulphide gas vigorously for about ten minutes.

Filter the precipitated sulphides through an 11-cm. filter, wash immediately to prevent oxidation and then insert the filter and contents into an 8-oz. distilling flask, the side-arm of which is bent down so as to connect with a vertical 8-in. Allihn condenser. Place a funnel in the neck of the flask, with the stem reaching below the side outlet connection, and pour through it 50 cc. of the copper, zinc chloride solution upon the sulphides. Insert a thermometer through the hole of a rubber stopper and arrange this in the neck of the distilling flask so that the thermometer bulb will be approximately $\frac{1}{4}$ in. from the bottom of the flask. Place a No. 2 beaker containing 40 cc. of cold water at the lower end of the condenser, so that the end is just sealed by the liquid. Heat the distilling flask gently with the naked flame of an alcohol lamp (having a chimney to prevent flame disturbance), or otherwise in such a manner that the sides of the flask will not be heated. Discontinue the heating when a temperature of 115° C. is reached.

Organic matter or elementary sulphur which may be observed in the distillate are without effect. SO_2 or other reductors affected by iodine will not be formed.

Unless the amount of arsenic is large, this distillation is sufficient, but if a quantity in excess of $\frac{1}{4}$ gram is suspected, add 25 cc. more of hydrochloric acid to the mixture in the flask and repeat the distillation.

Transfer the distillates to a No. 3 beaker, make alkaline with ammonia, then faintly acid with hydrochloric acid, add 2 grams of sodium acid carbonate and a little starch liquor, cool down to room temperature or cooler and titrate with the standard iodine solution to the usual blue tinge.

Antimony Determination.—Remove the stopper containing the thermometer from the flask and replace it with a stopper having a Walters separatory funnel reaching below the neck of the flask, but not into the liquid. The delivery end of the separatory funnel should be ground to a taper.

Place a No. 2 beaker, with water, as before, under the end of the condenser, so as to form a seal, heat the retort until the mass froths slightly and then allow hydrochloric acid to drop from the separatory funnel at the rate of one or two drops per second, and in such a manner as to avoid having any liquid remain in the tube below the bulb.

Maintain the temperature in the flask at the point at which the drops of acid cause only a slight spattering and no violent chugging in the condenser.

Use beakers, one after another, to seal the end of the condenser, and pass hydrogen sulphide into each until finally only a slight organic color is produced by the gas. Now, dilute the combined distillates containing antimony with an equal volume of water and pass in hydrogen sulphide for a few minutes. Filter the precipitated sulphide and wash quickly with warm water.

Insert filter and precipitate into an 8-oz. " copper flask," add three small pieces of quartz, a level-full Battersea cup of potassium acid sulphate (perhaps 10 grams) and 10 cc. of sulphuric acid. Bring to a boil and fume as directed in decomposing the ore. Cool with the flask on its side. When cool, add 50 cc. of water and 20 cc. of strong hydrochloric acid and heat gently until the cake has dissolved. Finally, boil a short time to expel any SO_2 present.

Cool to room temperature, dilute to about 200 cc. with cold water

and titrate with a standard solution of potassium permanganate—the usual solution standardized for iron. The Fe value of the permanganate, multiplied by 1.079, will give the Sb value. In titrating, take the first end-point that persists a short time, as the hydrochloric acid present gradually decomposes the excess of permanganate.

When the amount of arsenic in an ore will run several per cent, use a 1-gram charge in an 8-oz. flask with 7 grams of $KHSO_4$, one-eighth of a 9-cm. filter paper and 10 cc. of strong sulphuric acid. Conduct the heating and cooling as described for the larger amount of ore. After cooling, add 50 cc. of water, 2 to 3 grams of tartaric acid, boil until the melt is disintegrated, then add 10 cc. of strong hydrochloric acid and proceed as before.

DETERMINATION OF ARSENIC AND ANTIMONY, DISTILLATION METHOD *

Apparatus

Knorr Arsenic Still.—(E. Machlett & Sons, 143–147 East 23d Street, New York City.) The bottom of the distilling flask should project 1 in. through a round hole cut in a 5-in. square section of asbestos board.

Procedure

Arsenic.—Weigh 0.5 gram of sample into a 200-cc. casserole. Add 10 cc. of nitric acid, cover and digest on a hot plate for five minutes. Add 5 cc. of sulphuric acid. Boil to fumes and fume two minutes over a free flame. Add 5 cc. of phosphorus acid, again boil to fumes and fume two minutes over a free flame.

Remove the dropping funnel from the apparatus and substitute a Gooch funnel. Wash the contents of the casserole, after cooling, into the distilling flask, using 15 cc. of water. Place 20 cc. of hydrochloric acid in the casserole and set aside. Replace the dropping funnel in the apparatus, lubricating the ground glass with sulphuric acid and luting the joints between the flask and condenser in the same way.

Place 250-cc. beaker, containing 100 cc. of cold water, so that the tip of the condenser is $\frac{1}{2}$ in. below the surface of the water. Surround

* Method of the Selby Plant of the American Sm. & Ref. Co.

the beaker with running cold water. Pour the hydrochloric acid in the casserole through the dropping funnel into the flask. Close the stopcock and place 20 cc. of hydrochloric acid in the dropping funnel.

Apply a low flame to the bottom of the flask, and, as soon as the contents begin to boil, add hydrochloric acid from the dropping funnel at the rate of 1 drop in eight seconds, or 30 drops in four minutes. Continue the distillation for five to ten minutes.

Remove the beaker containing the distillate, add ammonia until slightly alkaline, then reacidify faintly with hydrochloric acid. Cool completely, add 5–10 grams of sodium acid carbonate and a little starch liquor, and titrate with standard iodine solution (approximately 1/10 normal) to the usual bluish tinge.

Iodine Solution.—12.7 grams of re-sublimed iodine, 20 grams of potassium iodide. Dissolve in a small amount of water and then dilute to 1 liter. To standardize, weigh out 0.2 gram of arsenious oxide of known arsenic content, run as an ore and finally titrate with the iodine solution.

Indicator Error.—Take 100 cc. of water in a beaker, add 20 cc. of hydrochloric acid, make slightly alkaline with ammonia, then faintly acid with hydrochloric acid. Cool thoroughly, add 5–10 grams of sodium acid carbonate and a little starch liquor. Titrate with the standard iodine solution to the usual blue tinge. Note the amount of iodine solution used and deduct this from all titrations.

Antimony.—Wash the residue remaining in the flask after the distillation of arsenious chloride, into a 600-cc. beaker. Cool, dilute to 500 cc. with cold water and titrate the Sb with standard potassium permanganate solution to the usual pink tinge. The permanganate used for iron titrations will serve. The Fe value multiplied by 1.079 will give the Sb value.

Notes.—If an ore contains much silica, bumping is likely to occur during the distillation. To avoid this, after fuming with sulphuric acid, cool, dilute with water, bring to a boil and filter off the silica. Take to fumes again and reduce with phosphorus acid.

Arsenic goes into solution in nitric acid as arsenic acid. This is reduced to arsenious acid by the phosphorus acid.

Phosphorus acid is oxidized to phosphoric acid by the sulphuric acid, the sulphuric acid being reduced to sulphurous acid, which volatilizes.

The prescribed mixture (10 cc. sulphuric acid, 20 cc. water and 20

cc. hydrochloric acid) gives the proper condition for the arsenic to distill over, while the antimony remains in the still.

The arsenic distills as arsenious chloride, most of it going over very quickly. The greater part of the time of the distillation is taken in sweeping out the apparatus.

Antimonious chloride does not distill over until the sulphuric acid begins to fume.

Sufficient sodium acid carbonate must be present during the arsenic titration to neutralize all hydriodic acid formed and still leave an excess of the salt.

DETERMINATION OF SULPHUR IN OILS

The sodium peroxide method was devised by Edinger (Zeit. Anal. Chem., Vol. 34, p. 362, 1895), and modified by Parr (Jour. Am. Chem. Soc., Vol. 30, p. 767, 1908) and has been further modified by Franks (Chem. Met. Eng., Vol. 25, p. 49, 1921). The following is a description of the method as modified by Franks:*

Sodium Peroxide Method.—This method employs the Parr sulphur bomb, made especially for the purpose. It may be obtained at supply houses.

Place in the bomb 1 measure (the measure is supplied with the bomb) of pure sodium peroxide (calorimeter quality), 1 gram of powdered potassium chlorate and 0.2 gram of powdered benzoic acid. Mix well by shaking and stirring. (When a large number of determinations are to be made it is best to prepare a quantity of this mixture, sufficient for all the determinations, and use a heaping measure for each determination. Care must be taken that the mixture is uniform.)

Weigh, as nearly as possible, 0.5 gram of the well-mixed oil into the bomb containing the above mixture. Use a medicine dropper and a small weighing bottle. By means of a thin glass rod, stir in the oil and thoroughly incorporate it with the peroxide mixture. This should be done as quickly as possible (best over glazed paper to catch any droppings), so that the peroxide will not be appreciably acted upon by the moisture in the air, and also to lessen any possible volatiliza-

* Professor A. J. Franks, Colo. School of Mines.

tion of the oil. With very volatile oils, such as gasoline, this procedure cannot be followed. Instead, weigh the oil with the use of a small, thin glass bulb, having a capillary neck that can be sealed after weighing. Break the bulb in the peroxide mixture just before placing the cap on the bomb. With such thin liquids stirring is not necessary; the liquid will penetrate through all parts of the mixture if a short time is allowed for this to take place.

Tightly close the bomb and hold it with a pair of crucible tongs in the blue flame of a Bunsen burner, to ignite the contents. When ignition occurs a slight kick will be felt, and the bomb will suddenly become red. As soon as this red glow is observed, immerse the bomb instantly in a cup of cold water to prevent decomposition of the rubber washer. When the bomb is quite cold, remove and open it, wiping it dry with a clean cloth. Remove the cap carefully and place the bomb gently on its side in a 400-cc. beaker. If any of the fusion adheres to the cap, rinse it into the beaker with the wash bottle. Add sufficient additional water to the beaker to make a total volume of 50–75 cc. Cover the beaker with a watch-glass and cautiously roll the bomb about at intervals until the fusion has completely dissolved, which usually requires only a few minutes. Occasionally the solution goes on very slowly, in which case it can be accelerated by the careful addition of a few drops of hydrochloric acid.

When solution is complete, carefully remove the bomb on a glass rod and rinse off the outside into the beaker, so as to permit handling with the fingers; then wash out the inside thoroughly. Now pour about 1 cc. of strong hydrochloric acid into the bomb and again wash it out well. This is to dissolve particles that sometimes stick to the bomb and also to cleanse the latter more effectually.

Now carefully make the solution just acid with strong hydrochloric acid. Unless caution is used there is likely to be loss by spattering, on account of the rapid evolution of carbon dioxide. A good plan is to run the acid in a thin stream down the side of the beaker, while constantly stirring with a glass rod. The neutral point can easily be detected; when it is reached, the precipitate of ferric hydroxide (always present) just dissolves, the solution becoming clear. Now add 5 cc. of saturated bromine water. This is to ensure complete oxidation of all the sulphur to sulphuric acid and all iron to the ferric condition. This would appear to be an unnecessary precaution, but experience has shown that unless it is taken the results are not con-

sistent and iron is almost always found in the subsequent barium sulphate precipitate.

Now add ammonia just to alkalinity. Much of an excess will necessitate tedious boiling off or neutralization later. Bring the solution to a vigorous boil, to coagulate the ferric hydroxide and expel the slight excess of ammonia. Filter the hot solution, washing with hot water. A small wad of absorbent cotton in the apex of the filter will facilitate filtration and washing. Three of four washings are sufficient if the percentage of sulphur is low; otherwise, wash thoroughly.

If all the excess ammonia has been boiled off, acidify the solution by the addition of 1 cc. of strong hydrochloric acid, dilute to about 225 cc., heat to boiling and add, very slowly, from a pipette, 5–10 cc. of a 10 per cent solution of barium chloride, the amount depending upon the expected amount of sulphur.

In case the excess ammonia has not been boiled off, it must be neutralized carefully with hydrochloric acid, with a piece of blue litmus paper as indicator. Then add 1 cc. of strong hydrochloric acid and proceed as above.

Continue the boiling until the precipitate is well formed, perhaps twenty minutes. About 200 cc. of liquid should remain. Allow to stand overnight and then filter the precipitate through a close 7-cm. paper (Munktell No. 00). Carefully wash precipitate and paper with a fine stream of cold water until free from chlorides, testing the filtrate from time to time with silver nitrate solution until no precipitate or cloudiness is obtained.

Ignite the damp filter and precipitate in a small (about No. 000) porcelain crucible at a dull red heat, until the carbon is completely burned. The residue of barium sulphate will be pure white if the procedure has been correctly followed. $BaSO_4 \times 0.1373 = S$.

At least two blanks should be run on each new lot of reagents, and the gross results corrected accordingly. If the blanks do not check closely they should be repeated, where accurate results are desired.

It is necessary to mix the oil and peroxide mixture with a glass rod to obtain a complete combustion of the organic matter. It is advisable to have the amount of oil weighed as close as possible to 0.5 gram. A larger amount (over 0.55 gram) will not be completely burned. If the amount is smaller, the errors are larger. Where very accurate results are not required it is not necessary to remove the iron with

ammonia. The presence of iron brings the results slightly high, and precise work therefore requires its absence. It is necessary to precipitate the barium sulphate from a boiling solution and to continue the boiling for some time, otherwise the precipitate will be finely divided and tend to run through the filter-paper.

It is always advisable to save and examine the filtrate from the barium sulphate precipitate. Even with extreme care and with the best filter-papers, a small amount of barium sulphate sometimes runs through, although the quantity is usually insignificant. In case it is evidently appreciable, it should be refiltered, through another filter, and this paper ignited with the first precipitate.

NITRIC ACID METHOD FOR DETERMINING SULPHUR IN OILS

This method has been developed by C. E. Waters,* whose description of it follows. According to the investigations of Franks,† it is neither as short nor as consistently accurate as the sodium peroxide method described above; but it is nevertheless an excellent method as an alternative, if the Parr bomb is not available.

Weigh from 0.5 to 2.0 grams of oil in a 100-cc. porcelain crucible, add 5 cc. of concentrated nitric acid which has been saturated with bromine, and at once cover with a watch-glass. When rather volatile oils, or those which smell of hydrogen sulphide, are analyzed, the crucible should be covered during the weighing, and each sample should be treated with the acid at once. and not be left until the series of weighings is finished.

Place on the steam-bath, but not in direct contact with the steam, and digest for thirty minutes or more, with an occasional gentle swirling of the contents of the crucible. Unless the mixture threatens to foam up to the cover, the crucible may now be heated by the direct steam for two or three hours. If there is much foaming, the digestion at moderate heat must be continued longer.

Remove the crucible from the bath, and when its contents have cooled somewhat, add cautiously, in small portions, 10 or 12 grams of anhydrous sodium carbonate. This is conveniently measured in a

* U. S. Bureau of Standards, Tech. Paper 177.

† A. J. Franks, Colo. School of Mines.

15-cc. crucible, rather than weighed. The first portions of soda often remain on top of the oily layer, so that the crucible must be tilted or swirled slightly to start the reaction. When about half the soda has been added, rinse the watch-glass cover with 1 or 2 cc. of warm water and leave it off. Pour in the rest of the soda. With a glass rod, about 3 mm. thick and 12 cm. long, thoroughly mix the contents of the crucible and spread the pasty mass around on the sides and half to two-thirds of the way to the top. The rod is left in the crucible, which is then placed on the steam bath, or in an air-bath at 100° C.

When its contents are dry enough, the crucible is placed in an inclined position on a wire triangle, and the ignition is started over a low flame. When more than 1 gram of oil has been taken, there is a tendency for it to burn too briskly, but this is easily controlled by judicious use of the stirring rod which scrapes the burning portion away from the rest. When part of the mass has burned white, more is worked into it, and so on until all of the organic matter is destroyed. It is necessary to hold the crucible with the tongs during this operation. Toward the end of the ignition, the flame may be increased somewhat, but it is rarely necessary to heat the crucible to redness. With care, a good crucible should last for many determinations. Of two crucibles which had been used for seventeen determinations each, and were still in almost perfect condition, one had lost just 100 mg., and the other 1.1 mg. less.

If a suitable muffle is available, the ignitions can be made at a temperature not above 550°. The glass rod should be removed and the crucible covered with a watch-glass. The principal danger is that the oil may start to burn at some point and the whole mass begin to glow in a few seconds. In this case the cover may be blown aside and loss by spattering occur. Under proper conditions, several ignitions can be made at one time.

According to the amount of oil taken, the mixture of sodium salts resulting from the combustion varies from granular to pasty when hot. After cooling, place the crucible upright in a 400-cc. beaker and fill it with distilled water. After a short time lay it on its side, cover the beaker and digest on the steam-bath. When the salts have dissolved, remove and rinse the crucible.

Filter the solution to remove specks of carbon, bits of the glass rod, etc. Acidify with concentrated hydrochloric acid, using Congo-red

paper as indicator, and add 2 cc. of acid in excess. The neutralization proceeds more safely if nearly the required amount of acid is put in the covered beaker into which the solution is filtered. It is safe to use 10 cc. of acid for this, but the exact amount cannot be stated, because the total amount of carbonate and nitrate to be neutralized depends upon how much oil was taken. The acidified filtrate and wash water should have a volume of about 175 cc. Heat on the steam-bath, add 10 cc. of barium chloride solution (containing 100 grams of crystallized salt in 1 liter), and digest on the bath until the supernatant liquid is clear. If possible, delay the filtration until the next day.

A blank should be run with every new lot of reagents. An ignition is made just as if oil were present, because the flame may contain enough sulphur to be corrected for. Even when the correction amounts to several milligrams, almost no precipitate may be seen before the solution has stood for several hours.*

It is needless to describe how the barium sulphate is filtered off, washed and ignited. (See peroxide method.—A. H. L.)

Note.—For sources of error, correction for occlusion and general discussion, see original paper.

The method has been used for coal, lignite, peat, organic substances, etc.

Notes on the Above Method by Franks.†—Instead of the 100-cc. crucible recommended by Waters, I prefer a 75- to 100-cc. porcelain casserole. Waters directs to use 0.5 gram to 2 grams of oil. I find that 1 gram gives good results; 2 grams is too much. I find, also that 12 grams of anhydrous sodium carbonate are required. Use of a smaller amount causes too vigorous combustion during the fusion process, which results in sputtering and inconsistent results. The use of more than 12 grams makes combustion difficult and the carbon is not easily burned off.

I usually prefer to ignite over a wire gauze. The naked flame tends to cause overheating and hence too sudden combustion, which causes sputtering and loss of sulphur. The best way to make the fusion is to

* It is not necessary to have the solution boiling when the barium chloride is added, or to digest the precipitate with the boiling solution. Hillebrand (Anal. of Carb. Rocks, Bull. 700, U. S. Geol. Surv., p. 232) says "at a boiling heat or on the steam-bath." It is much more convenient to use the steam-bath, and there is no danger of loss by bumping; also, as pointed out by Hillebrand, there can be no contamination by sulphur from the flame.

† Private communication.

start it carefully on one side of the casserole. As the mass ignites it should be rapidly stirred at the point of combustion and the unburned material gradually worked into this heated zone. If the ignition is allowed to start at the bottom of the casserole, where most of the mass lies, it is liable to begin suddenly and violently and occasion loss. Also, the high temperature developed by this sudden ignition materially shortens the life of the casserole.

In the precipitation of barium sulphate, I always bring the solution to a boil before adding the barium chloride solution. The barium sulphate precipitate is allowed to stand overnight and is filtered the next day through a 7-cm. (No. 00, Munktell) paper. The precipitate is ignited in a No. 000 porcelain crucible.

BISMUTH IN ORES*

Run down 10 grams of the ore with sufficient litharge and the necessary fluxes to produce a 10-gram lead button. Roll the lead button into a ribbon and dissolve it in a mixture of 25 cc. of nitric acid and 50 cc. of water, by warming. Heat the solution nearly to boiling and neutralize with ammonia, finally adding it, drop by drop, until the precipitate formed has redissolved. Now add ½ cc. of hydrochloric acid and dilute with 100 cc. of water. Bring to a boil and then allow to stand hot, but not boiling, for an hour and a half. Filter through a close filter and wash with hot water. Dissolve the precipitate on the filter with warm dilute nitric acid (1 : 1), using as little as possible. Receive the filtrate in an 8-oz. flask. Cool, add 5 cc. of sulphuric acid and boil to fumes. Cool, add 25 cc. of water and heat to boiling. Add 10 cc. of alcohol and cool under tap. Filter off the lead sulphate without unnecessary delay and wash it well with dilute sulphuric acid (1 : 10). Receive the filtrate in a beaker. Dilute it somewhat with water and pass in hydrogen sulphide to saturation. Filter off the bismuth sulphide, washing with water. Dissolve the sulphide on the filter with hot dilute nitric acid (1 : 1). Receive the solution in a beaker. Neutralize with ammonia and then add a slight excess of ammonium carbonate. Boil ten to fifteen minutes and allow to settle. Filter, wash precipitate with hot water and then

* Method of Arkansas Valley Plant of the American Sm. & Ref. Co.

dry. Ignite in a weighed porcelain crucible at a low heat. Cool, moisten the residue with nitric acid and again dry and ignite. Weigh as bismuth trioxide. Bi_2O_3 multiplied by 0.8965 = Bi.

This method is for ores containing only a few tenths of a per cent of bismuth. With ores containing 2–3 per cent, it is better to treat 0.5 gram without running into a lead button.

If antimony interferes, separate by precipitating the bismuth with hydrogen sulphide from an alkaline solution.

BISMUTH IN BISMUTH BULLION *

Standard Solutions

Silver Nitrate.—Dissolve 1.038 grams of pure silver in 10 cc. of nitric acid and dilute to 1 liter.

1 cc. = 0.002 gram Bi.

Ammonium Thiocyanate.—Dissolve 0.732 gram and dilute to 1 liter.

1 cc. = 1 cc. of the silver solution. Determine the relation exactly by titration, using ferric alum as indicator. (See CHLORINE, 3.)

Procedure

Up to 25 per cent, weigh out 10 grams and dissolve in 15 cc. of nitric acid.

From 25 to 50 per cent, 5 grams in 10 cc. of nitric acid.

Over 50 per cent, 2 grams in 10 cc. of nitric acid.

Weigh the determined amount into a 600-cc. beaker. Add 50 cc. of water and the required amount of nitric acid plus 1 gram of tartaric acid. Warm until dissolved and then dilute to 500 cc. with hot water. Boil the solution and add 5 cc. of 85 per cent phosphoric acid solution, previously somewhat diluted. Continue the boiling for five to ten minutes and then allow to settle in a warm place. Filter on a close paper and wash two or three times with hot water. Dissolve the precipitate through the filter into the original beaker with hot dilute (1 : 1) hydrochloric acid. Be sure that none of the bismuth salt remains in the paper. Neutralize the filtrate with ammonia, cautiously, until a faint permanent cloud is produced. Now add 1 cc. of

* Omaha Plant, Amer. Sm. & Ref. Co.

1 : 1 nitric acid and dilute to 500 cc. with hot water. The bismuth precipitates as BiOCl. Allow to settle overnight in a warm place and then filter on a close paper, washing thoroughly with hot water until free from soluble chlorides.

Dissolve the precipitate through the filter with hot 1 : 1 nitric acid, washing the paper well with the same acid but not using an undue excess. Receive the filtrate in a 250-cc. flask. Cool completely and then from a burette, run in an excess of the standard silver nitrate solution. Shake well to coagulate the silver chloride and then titrate the excess of silver nitrate solution with the standard ammonium thiocyanate solution, with ferric alum as indicator (see CHLORINE, 3).

This shows the number of cubic centimeters of silver solution consumed by the bismuth, from which the per cent may be calculated.

It is claimed that this is an excellent method, with a tendency, however, toward slightly low results.

BISMUTH IN BISMUTH BULLION *

Weigh 2 grams into a 600-cc. beaker. Add 10 cc. of nitric acid and 10 cc. of water. Warm until dissolved and then dilute to 500 cc. with hot water. Heat to boiling, add 5 cc. of syrupy phosphoric acid and continue the boiling for five to ten minutes. Allow to settle in a warm place, and then filter the bismuth phosphate on a close filter, washing several times with hot water. Dissolve the precipitate on the filter with hot 1 : 1 hydrochloric acid, receiving the filtrate in an 8-oz. "copper flask." Add 5 cc. of sulphuric acid and boil to dense fumes. Cool sufficiently and then dilute, first with cold water and then with hot water, to 150 cc. Boil a few minutes and then filter off the lead sulphate, washing with dilute sulphuric acid (1 : 10). Receive the filtrate in a beaker. Add 1 or 2 pieces of stout sheet aluminum, cover the beaker and boil down to about 30 cc., then dilute to about 150 cc. and again boil a few minutes. Filter the precipitated metallic bismuth through a weighed Gooch crucible, washing first with hot water and then with alcohol. Dry at 100° C. to constant weight and

* Arkansas Valley Plant, Amer. Sm. & Ref. Co.

weigh as Bi. The results are likely to be slightly high. (This method is slightly modified from the original description.)

CADMIUM IN SPELTER*

Dissolve 25 grams of sample in a No. 4 beaker in a mixture of 34 cc. of strong sulphuric acid and 250 cc. of water. In the case of very pure zinc it may be necessary to add a few drops of very dilute platinum chloride solution, from time to time, to hasten the action. The above amount of acid is approximately 12.5 cc. more than is required to dissolve 25 grams of zinc, and therefore about 12.5 cc. of free acid will remain in the solution. Lead, copper and probably a small amount of cadmium remain undissolved. Pay no attention to the flocculent residue, but make sure that all the zinc is dissolved. Add 15 grams of solid ammonium sulphate to the warm liquid and pass in hydrogen sulphide for ten minutes. Allow to stand, warm, for half an hour, and then pass in hydrogen sulphide for ten minutes more. All the cadmium is precipitated as sulphide, together with considerable zinc sulphide, lead and copper.

Filter on a 12½-cm. paper and wash three or four times with warm water. The filtration is rather slow, but proceeds steadily enough if a good column is established in the funnel stem. Return the precipitate, paper and all, to the beaker in which the precipitation was made, add 10 cc. of strong sulphuric acid and 10 cc. of strong nitric acid, cover the beaker and heat until sulphuric acid fumes are given off. Remove the beaker from the heat, and to the hot, but not strongly fuming, liquid add a few more cubic centimeters of strong nitric acid and again boil to fumes.

Repeat the addition of nitric acid as above until the paper is completely consumed. This usually requires about three additions of acid with intermediate fuming. The whole operation requires about three-quarters of an hour. It is important that the filter-paper shall be completely oxidized. Cool the solution, dilute with water to 200 cc. and boil a short time. Allow the solution to cool and the lead sulphate to separate. Filter out the precipitate, washing once or twice with dilute sulphuric acid (1 : 20).

* Ledoux & Co., New York.

The liquid now contains about 10 cc. of sulphuric acid in 200 cc. Add 10 grams of ammonium sulphate and pass hydrogen sulphide into the warm solution exactly as before. Cadmium comes down as sulphide, practically free from zinc. Filter the cadmium sulphide on a 9-cm. paper and wash it three or four times with warm water. Dissolve paper and precipitate in a No. 2 beaker with 5 cc. sulphuric acid and 5 cc. nitric acid, and evaporate to fumes. Repeat the evaporation with additions of nitric acid, as described above, until the paper is destroyed, then cool, add 5 cc. of water and again evaporate to fumes. Repeat the addition of water and evaporation to fumes a second time.

These last evaporations are to expel all nitric acid. The work should be done in a place free from heavy nitric fumes, since even a trace of nitric acid interferes with the electrolysis of cadmium. Add 25 or 30 cc. of water to the sulphuric acid residue and heat until all soluble salts are dissolved. Cool, neutralize the excess of free sulphuric acid with ammonia, using litmus paper as an indicator, and then add 4.5 cc. of dilute (1 : 2) sulphuric acid. This gives a solution containing 1.5 cc. of free sulphuric acid. Dilute with water to 125 cc. and electrolyze (preferably overnight), using a current of 0.1 ampere and 2.6 volts to about 10 sq. in. of cathode surface (one side).

The cathode is a perforated platinum cylinder $2\frac{1}{8}$ in. high by $1\frac{1}{2}$ in. in diameter. Under the conditions given, cadmium is precipitated free from zinc, even though there be a trace of zinc in the solution. Copper also comes down with the cadmium.

After weighing the cathode, dissolve the deposited metal in a few drops of dilute nitric acid, boil, make alkaline with ammonia, dilute to 10 cc., and compare the color with similar solutions containing known amounts of copper. The two or three tenths of a milligram of copper usually present may be estimated closely in this way.

If the laboratory is not equipped with electrolytic apparatus, cadmium may be determined by weighing as sulphate. Since two precipitations with hydrogen sulphide, as described, may not remove all of the zinc (and will not unless the work is done with great care), a third precipitation with hydrogen sulphide should be made. This is unnecessary when the electrolytic method is used, because, under the conditions given, small amounts of zinc remain in the electrolyte. After the third precipitation of the cadmium sulphide, wash it with water, dissolve it in hot dilute nitric acid, add $\frac{1}{2}$ to 1 cc. of sulphuric

acid and evaporate to dryness in a porcelain crucible, then ignite at a low temperature to constant weight. Copper will be present here also. It should be estimated colorimetrically, calculated to $CuSO_4$ and deducted from the weight.

Note that the presence of a large amount of ammonium sulphate is essential to good results in precipitating cadmium with hydrogen sulphide from sulphuric acid solutions. The proportions of acid and water are also important in obtaining clean separations. Those given above should be strictly adhered to.

DETERMINATION OF NITROGEN IN SODIUM NITRATE

The following modification of Devada's method was developed by L. B. Skinner, formerly General Manager of the Western Chemical Manufacturing Co.

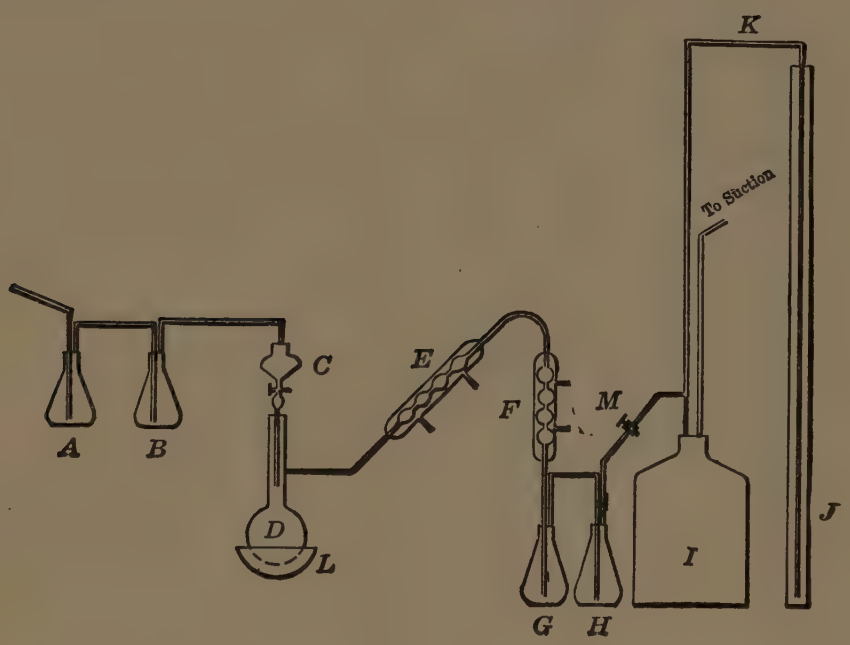

FIG. 24.

Referring to the accompanying diagram:

A is a 250-cc. flask, containing about 2 in. of strong sulphuric acid.

B is a 250-cc. flask, containing about 2 in. of a 30 per cent solution of sodium hydroxide.

C is a long-stemmed separatory funnel.

D is a 1-liter flask, in which the reactions take place.

E is an 8-in. Allihn condenser, the bulb packed loosely with glass wool and to be heated by steam.

F is an 8-in. bulb condenser, cooled with water.

G is a 250-cc. flask, containing standard sulphuric acid, for the absorption of ammonia given from the nitrate.

H is a safety flask used in connection with *G*, also containing a solution of standard acid.

I is a 15- to 20-liter bottle, to act as a reservoir for minus pressure, so that at the height of the reaction in the flask *D*, there will always be a suction on the whole apparatus.

J is a 6-ft. length of 1-in., or $1\frac{1}{4}$-in. glass tube, which is filled with water to about 1 in. from the top. A tube *K* passes to the bottom of *J*, thus causing *J* to act as a gauge for the suction on the apparatus.

A filter pump, having a capacity of about 10 cu. ft. of air per minute, is used for suction. If this were connected directly with the apparatus, without the interposition of the reservoir and gauge, there would be danger of some of the flasks collapsing from the high suction.

L is a 6-in. evaporating dish, which is to be filled with cold water at the beginning of the reaction in *G*.

Assembling the Apparatus.—Rinse all parts of the apparatus with C. P. water. Put 2 in. of strong sulphuric acid in *A*, and 2 in. of 30 per cent sodium hydroxide solution in *B*. Having the bulbs in *E* packed loosely with glass wool, connect *E* so that the steam will enter at the top and discharge at the bottom. Connect *F*, arranging it so that cold water will enter at the bottom and discharge at the top. Run into *G*, from a burette, an excess of about 5 cc. of the standard sulphuric acid, and put 10 cc. of the standard acid into *H*. One cubic centimeter of the standard acid is equivalent to about 0.02 gram of sodium nitrate, and, as an amount of nitrate solution containing 2 grams of the nitrate to be tested is taken for the analysis, the equivalent amount of the standard sulphuric acid would be about 100 cc., if the nitrate were pure. Ordinarily, 95–99 cc. of the acid are sufficient to put in *G*. Now dilute the standard acid in *G* and *H* with C. P. water to a depth of 2 in. in each case. Connect *G* and *H* as shown in the diagram. Close the stopcock *M* and start the suction.

Procedure.—Weigh out 100 grams of the nitrate. Dissolve in C. P. water, make up to 500 cc. and note the temperature of the solution. Transfer the solution from the measuring flask to a dry bottle large enough to allow the solution to be well mixed by shaking. After

shaking well, pour part of the solution back into the measuring flask, using the same funnel as when pouring from the flask into the bottle, and rinse the flask well with the solution in this way. This is done in order to be sure of having an evenly mixed solution.

Weigh out 6 grams of the alloy and place in the reaction flask *D* by the aid of a dry, long-stemmed funnel, so as to avoid getting any of the alloy on the sides of the flask. Now put exactly 10 cc. of the nitrate solution into the flask *D*, having the solution at the same temperature it was in the 500-cc. flask. It is best to measure the nitrate solution from a 50-cc. burette, which has been checked against the 500-cc. flask. Connect the flask *D* and fill the dish *L* with cold water.

Place 50 cc. of a 20 per cent caustic soda solution (free from all nitrogen compounds) in the top of the separatory funnel *C*, and replace the stopper in the top of *C*, having the cock *R* closed during this time. By this time the air in *I* will be sufficiently exhausted to cause the gauge *J* to begin to work. Now open the cock *M* and allow the suction to draw on the main apparatus until the gauge *J* begins to work again. Make sure that there are no leaks in the stoppers or connections; if there are no such leaks, there will be no bubbles passing through *G* and *H* after the apparatus has once been exhausted. Everything being ready, open the cock *R* and allow the caustic solution in *C* to run into *D*, closing *R* as soon as the caustic has passed through.

A stream of cold water is kept running into *L* until most of the reactions are finished. After the reaction has subsided until there is no great violence in the flask, remove *L* and allow the reaction to continue slowly until it is complete, which is shown by the cessation of bubbles in *G* and *H*. It should require from thirty to forty-five minutes for the completion of the reaction in the flask *D*. When this stage is reached, place a small flame under *D* and bring the contents to boiling. As soon as the flame is placed under *D*, turn dry steam into the condenser *E*. Allow the solution to boil slowly until there is no more gas passing through the flasks *G* and *H*, adding more hot water to *D* when necessary. Now open the stopcock *R* and allow a stream of air to pass through the whole apparatus at the rate of about four bubbles per second. Continue this for forty-five minutes, then separate the connection at the top of *F* and rinse *F* and all the tubes connecting *F*, *G* and *H* into *G* and *H*.

Transfer the contents of *G* and *H* into a large beaker and titrate the excess of acid with the standard alkali.

Cochineal may be used as indicator. Allen * recommends making the solution in the beaker up to a volume of 500 cc., and adding 1 cc. of methyl red solution † as indicator. The end-point in this case is straw-yellow.

Duplicate results should check within 0.05 of 1 per cent, at least. The principal precaution to observe is not to allow the reaction in the flask *D* to proceed too rapidly at the outset, as this might occasion a loss of ammonia. The reaction may be regulated by passing cold water into the dish *L*. Another necessary precaution is to always have a minus pressure in the entire apparatus, after the caustic solution has once been transferred from *C* to *D*.

The above method of analysis gives all the nitrogen, whether existing as nitrate or nitrite. Therefore, if it is desired to obtain the nitrate only, it will be necessary to titrate part of the 500-cc. solution with potassium permanganate for nitrite and deduct the equivalent of the nitrite found from the total nitrate indicated by the analysis.

Standard Solutions.—The standard sulphuric acid solution is made so that 1 cc. will equal about 0.02 gram of $NaNO_3$. This strength is approximated by adding about 12.1 grams of ordinary C. P. sulphuric acid to 1 liter of distilled water. To standardize, weigh an amount of potassium nitrate equivalent to 2 grams of sodium nitrate. If the potassium nitrate were absolutely pure and dry, 2.3782 grams would equal 2 grams of sodium nitrate. The amount of impurity in the potassium nitrate should be determined and allowed for by weighing out a quantity equivalent to 2.3782 grams of the pure salt. The ordinary C. P. potassium nitrate usually contains from 0.01 to 0.03 of 1 per cent of impurities other than moisture. Before testing or using, it should be dried for two hours at 240° C. A large amount may be dried at one time and kept in a well-stoppered bottle.

Dissolve the weighed potassium nitrate in the smallest possible amount of water. Place the alloy in the reaction flask *D*, add the potassium nitrate solution and proceed with the process identically as directed for the regular analysis. The value of 1 cc. of the sulphuric acid, in terms of sodium nitrate, is thus determined.

* W. S. Allen, General Chemical Company.

† Allen recommends 0.025 gram of methyl red dissolved in 200 cc. of 95 per cent. alcohol. All water used in the analysis must be well boiled, as this indicator is sensitive to CO_2.

The standard alkali solution for titrating the excess of acid above what was required to neutralize the ammonia evolved, is prepared by dissolving 9.5 grams of C. P. NaOH in 1 liter of water. Check the alkali solution against the standardized sulphuric acid and finally bring it to the point at which 1 cc. will equal 1 cc. of the standard acid.

In case C. P. potassium nitrate for standardizing cannot be obtained, it is satisfactory to use absolutely C. P. nitric acid, titrating the same with a standard solution of caustic soda which is absolutely free from any nitrogen compound. After the titration is finished, evaporate the solution on a water-bath to a volume of 5 to 8 cc. and then transfer it to the reaction flask *D*, containing the alloy, proceeding from this point precisely as described for the regular analysis. The amount of nitric acid taken should be approximately equivalent to 2 grams of sodium nitrate. The titration will show its exact equivalent.

The Alloy.—This is of the composition given by Devada and consists of 5 parts zinc, 45 parts aluminum and 50 parts copper. The melt is made in a graphite crucible with a well-fitting cover. Skinner's directions are, to melt the copper, then to add the aluminum, and finally to add the zinc to the melted copper and aluminum. Stir the melted alloy well with an iron rod and then pour it into a dry cold mold. Grind the cold alloy until it passes through a 60-mesh screen. Keep the ground alloy in a well-stoppered bottle.

ASSAY FOR PLATINUM AND PALLADIUM

Run usual crucible assay for gold, using perhaps five crucibles with one assay ton of ore in each crucible. Add a little silver foil to each crucible so that there shall be at least 20 parts of silver to 1 part of platinum.

After cupellation, flatten the silver buttons and place all together in a porcelain crucible.

Method A.—Add about 10 cc. of strong sulphuric acid and keep almost at boiling point for about thirty minutes. Cool, decant acid into a beaker and then repeat the parting and decanting. Wash the residue carefully several times, decanting into the same beaker. Reserve the gold and platinum residue in the crucible.

Sufficiently dilute the washings in the beaker and pass them through a small ashless filter to catch any fine specks possible present. Pass the filtrate through a similar filter as a blank. Wash both filters well with hot water. Reserve the filtrate containing the palladium.

Ignite the first filter with the reserved gold and platinum residue and then weigh.

Similarly ignite the second filter in a porcelain crucible and deduct the weight of the residue from that of the gold and platinum residue. This gives the Au+Pt.

Wrap the Au−Pt residue in 8 grams of lead foil, adding silver so as to have at least 12 parts silver to 1 part platinum, and cupel. Flatten the resulting silver button and part with nitric acid containing 46 per cent of 1.42 sp gr. acid. The washed and ignited residue gives the Au (the Pt being here shown by difference).

Add the washings to the reserved washings, which may meanwhile have been evaporating. Add salt to precipitate the silver, which, after the usual procedure, is to be filtered off and discarded.

Neutralize the filtrate (containing Pt and Pd) with ammonia, reacidify slightly with hydrochloric acid and pass in hydrogen sulphide for thirty minutes, finally allowing to stand over night. Now filter, wash, ignite at a moderate temperature and weigh. Run blank on filtrate and deduct. This gives combined Pt and Pd.

Treat residue by warming ten minutes with strong nitric acid. Dilute, filter and wash. Ignite and weigh residue as Pt.

Neutralize filtrate with ammonia, reacidify with hydrochloric acid and precipitate with hydrogen sulphide precisely as before, except that several hours' standing is usually sufficient. Filter, wash, ignite and weigh as Pd. The weight should check that obtained above by difference.

Method B.—Instead of parting with sulphuric acid, use nitric acid of 1.2 sp. gr. Weigh the residue as Au. The filtrate and washings contain the Pt and Pd. Remove and discard the silver as above. Neutralize the filtrate with ammonia, add hydrochloric acid and separate the Pt and Pd as above.

TABLES

RELATION OF BAUMÉ DEGREES TO SPECIFIC GRAVITY, FOR LIQUIDS LIGHTER THAN WATER, AT 60° F.

Baumé.	Specific Gravity.	Baumé.	Specific Gravity.	Baumé.	Specific Gravity.	Baumé.	Specific Gravity.
10	1.0000	31	0.8695	52	0.7692	73	0.6896
11	0.9929	32	0.8641	53	0.7650	74	0.6863
12	0.9859	33	0.8588	54	0.7608	75	0.6829
13	0.9790	34	0.8536	55	0.7567	76	0.6796
14	0.9722	35	0.8484	56	0.7526	77	0.6763
15	0.9655	36	0.8433	57	0.7486	78	0.6730
16	0.9589	37	0.8383	58	0.7446	79	0.6698
17	0.9523	38	0.8333	59	0.7407	80	0.6666
18	0.9459	39	0.8284	60	0.7368	81	0.6635
19	0.9395	40	0.8235	61	0.7329	82	0.6604
20	0.9333	41	0.8187	62	0.7290	83	0.6573
21	0.9271	42	0.8139	63	0.7253	84	0.6542
22	0.9210	43	0.8092	64	0.7216	85	0.6511
23	0.9150	44	0.8045	65	0.7179	86	0.6481
24	0.9090	45	0.8000	66	0.7142	87	0.6451
25	0.9032	46	0.7954	67	0.7106	88	0.6422
26	0.8974	47	0.7909	68	0.7070	89	0.6392
27	0.8917	48	0.7865	69	0.7035	90	0.6363
28	0.8860	49	0.7821	70	0.7000	95	0.6222
29	0.8805	50	0.7777	71	0.6965		
30	0.8750	51	0.7734	72	0.6930		

RELATION OF BAUMÉ DEGREES TO SPECIFIC GRAVITY FOR LIQUIDS HEAVIER THAN WATER, AT 60° F.

Baumé.	Specific Gravity.	Baumé.	Specific Gravity.	Baumé.	Specific Gravity.	Baumé.	Specific Gravity.
0	1.0000	18	1.1417	36	1.3303	54	1.5934
1	1.0069	19	1.1508	37	1.3426	55	1.6111
2	1.0140	20	1.1600	38	1.3551	56	1.6292
3	1.0211	21	1.1694	39	1.3679	57	1.6477
4	1.0284	22	1.1789	40	1.3810	58	1.6667
5	1.0357	23	1.1885	41	1.3942	59	1.6860
6	1.0432	24	1.1983	42	1.4078	60	1.7059
7	1.0507	25	1.2083	43	1.4216	61	1.7262
8	1.0584	26	1.2185	44	1.4356	62	1.7470
9	1.0662	27	1.2288	45	1.4500	63	1.7683
10	1.0741	28	1.2393	46	1.4646	64	1.7901
11	1.0821	29	1.2500	47	1.4796	65	1.8125
12	1.0902	30	1.2609	48	1.4948	66	1.8354
13	1.0985	31	1.2719	49	1.5104	67	1.8589
14	1.1069	32	1.2832	50	1.5263	68	1.8831
15	1.1154	33	1.2946	51	1.5426	69	1.9079
16	1.1240	34	1.3063	52	1.5591	70	1.9333
17	1.1328	35	1.3182	53	1.5761		

TABLE OF MEASURES AND WEIGHTS

Measures of Capacity

A. Dry Measure

1 bushel = 2150.42 cubic inches.
1 " = the volume of 77.627 pounds of distilled water at 4° C.
Legal: 1 liter = 0.908 quart.
1 bushel = 4 pecks = 8 gallons = 32 quarts = 35.24229 liters.
1 peck = 2 gallons = 8 quarts = 8.81057 liters.
1 gallon = 4 quarts = 4.40528 liters.
1 quart = 1.10132 liters.

B. Liquid Measure

1 U. S. gallon = 231 cubic inches.
1 gallon = the volume of 8.3388822 pounds = 58378 troy grains of distilled water at 4° C. (Stillman, Engineering Chemistry.)
1 " = 58318 grains of water at 62° F. (U. S. Phar.)
1 " = 58334.9+grains of pure water at 60° F., weighed in air at 60° F., at barometric pressure of 30 inches of mercury. (Mason, Examination of Water.)
Legal: 1 liter = 1.0567 quart = 0.26417 gallon.
1 gallon = 4 quarts = 8 pints = 32 gills = 3.78544 liters.
1 quart = 2 pints = 8 gills = 0.94636 liter.
1 pint = 4 gills = 0.47318 liter.
1 gill = 0.118295 liter.
1 cubic foot = 7.48 gallons = 28.315 liters = 62.42 pounds of water at 60° F. (Stillman.)
1 cubic foot of water at 62° F. = 62.355 pounds avoirdupois = 28,320 grams.
1 cubic inch of water at 62° F. = 0.0361 pound avoirdupois = 16.387 grams. (Watts' Dictionary, V, 1010.)

Linear Measure

1 yard = 0.91440 meter.
1 foot = 0.30480 meter.
1 inch = 0.0254 meter.
39.37 inches = 1 meter.

Weights

1 grain troy = 0.0648004 gram.
1 pound troy = 0.822857 pound avoirdupois.
1 pound avoirdupois = 7000 grains troy = 1.215279 pounds troy.

Troy Weight

1 pound = 12 oz. = 240 pwts. = 5760 grains = 373.2418 grams.
1 oz. = 20 pwts. = 480 grains = 31.1035 grams.
1 pwt. = 24 grains = 1.5552 grams.
1 grain = 0.0648 gram.
1 gram = 15.432 troy grains.

Avoirdupois Weight

1 ton = 20 hundredweight = 2240 pounds = 1016.04 kilograms.
1 hundredweight = 112 pounds = 50.80 kilograms.
1 pound = 16 ounces = 256 drams = 7000.00 grains = 453.5900 grams.
1 ounce = 16 drams = 437.50 grains = 28.3495 grams.
1 dram = 27.34 grains = 1.7718 grams.
1 net ton = 2000 pounds = 29166⅔ ozs. troy = 907.19 kilograms.

Metric Ton

1 metric ton = 1000 kilograms.

CONVERSION OF THERMOMETER READINGS

To convert Fahrenheit to Centigrade, subtract 32 and multiply by $\frac{5}{9}$.
To convert Centigrade to Fahrenheit, multiply by $\frac{9}{5}$ and add 32.

BEAKER NUMBERS AND CORRESPONDING CAPACITIES

Number.	Capacity, cc.
000	15
00	35
0	55
1	100
2	150
3	250
4	350
5	500
6	700
7	900
8	1500
9	2000
10	2600

PERCENTAGE SOLUTIONS

In this book the percentage of a salt in a solution is taken as the weight in grams in 100 cc. of the solution. This, of course, does not express the actual percentage correctly, but the system is easily understood and is used for convenience. Thus, a 10 per cent solution of a salt means 10 grams dissolved in the liquid and made up to 100 cc.

INTERNATIONAL ATOMIC WEIGHTS, 1921

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminum	Al	27.1	Mercury	Hg	200.6
Antimony	Sb	120.2	Molybdenum	Mo	96.0
Argon	A	39.9	Neodymium	Nd	144.3
Arsenic	As	74.96	Neon	Ne	20.2
Barium	Ba	137.37	Nickel	Ni	58.68
Bismuth	Bi	208.0	Niton	Nt	222.0
Boron	B	10.9	Nitrogen	N	14.008
Bromine	Br	79.92	Osmium	Os	190.9
Cadmium	Cd	112.4	Oxygen	O	16.0
Caesium	Cs	132.81	Palladium	Pd	106.7
Calcium	Ca	40.07	Phosphorus	P	31.04
Carbon	C	12.005	Platinum	Pt	195.2
Cerium	Ce	140.25	Potassium	K	39.1
Chlorine	Cl	35.46	Praseodymium	Pr	140.9
Chromium	Cr	52.0	Radium	Ra	226.0
Cobalt	Co	58.97	Rhodium	Rh	102.9
Columbium (Niobium)	Cb	93.1	Rubidium	Rb	85.45
Copper	Cu	63.57	Ruthenium	Ru	101.7
Dysprosium	Dy	162.5	Samarium	Sa	150.4
Erbium	Er	167.7	Scandium	Sc	45.1
Europium	Eu	152.0	Selenium	Se	79.2
Fluorine	F	19.0	Silicon	Si	28.3
Gadolinium	Gd	157.3	Silver	Ag	107.88
Gallium	Ga	70.1	Sodium	Na	23.0
Germanium	Ge	72.5	Strontium	Sr	87.63
Glucinum (Beryllium)	Gl	9.1	Sulphur	S	32.06
Gold	Au	197.2	Tantalum	Ta	181.5
Helium	He	4.0	Tellurium	Te	127.5
Holmium	Ho	163.5	Terbium	Tb	159.2
Hydrogen	H	1.008	Thallium	Tl	204.0
Indium	In	114.8	Thorium	Th	232.15
Iodine	I	126.92	Thulium	Tm	168.5
Iridium	Ir	193.1	Tin	Sn	118.7
Iron	Fe	55.84	Titanium	Ti	48.1
Krypton	Kr	82.92	Tungsten	W	184.0
Lanthanum	La	139.0	Uranium	U	238.2
Lead	Pb	207.2	Vanadium	V	51.0
Lithium	Li	6.94	Xenon	Xe	130.2
Lutecium	Lu	175.0	Ytterbium (Neoytterbium)	Yb	173.5
Magnesium	Mg	24.32	Yttrium	Yt	89.33
Manganese	Mn	54.93	Zinc	Zn	65.37
			Zirconium	Zr	90.6

CHEMICAL FACTORS AND THEIR LOGARITHMS

	Weighed.	Required.	Factor.	Log.*
Aluminum	Al_2O_3	Al	0.5303	9.7245
	$AlPO_4$	Al_2O_3	0.4185	9.6217
Antimony	Sb_2O_4	Sb	0.7897	9.8975
Arsenic	As_2S_3	As	0.6091	9.7847
	"	As_2O_3	0.8040	9.9053
	$Mg_2As_2O_7$	As	0.4827	9.6837
	"	As_2O_3	0.6372	9.8043
	"	As_2O_5	0.7403	9.8694
Barium	$BaSO_4$	Ba	0.5885	9.7697
	"	BaO	0.6570	9.8176
	$BaCO_3$	Ba	0.6960	9.8426
	"	BaO	0.7771	9.8905
	$BaCrO_4$	Ba	0.5422	9.7341
	"	BaO	0.6053	9.7820
Bismuth	Bi_2O_3	Bi	0.8965	9.9526
	BiOCl	Bi	0.8017	9.9040
	"	Bi_2O_3	0.8941	9.9513
Bromine	AgBr	Br	0.4256	9.6290
	"	HBr	0.4309	9.6344
Cadmium	CdO	Cd	0.8754	9.9422
	CdS	Cd	0.7780	9.8910
	"	CdO	0.8888	9.9488
	$CdSO_4$	Cd	0.5392	9.7317
Calcium	CaO	Ca	0.7146	9.8541
	$CaCO_3$	Ca	0.4004	9.6025
	"	CaO	0.5603	9.7484
	$CaSO_4$	Ca	0.2944	9.4689
	"	CaO	0.4119	9.6148
Carbon	CO_2	C	0.2727	9.4357
Chlorine	AgCl	Cl	0.2474	9.3934
	"	HCl	0.2543	9.4053
	Ag	Cl	0.3287	9.5168
	"	HCl	0.3380	9.5290
Chromium	Cr_2O_3	Cr	0.6842	9.8352
	"	CrO_3	1.3158	0.1192
	"	CrO_4	1.5257	0.1834
	$PbCrO_4$	Cr	0.1609	9.2067
	"	CrO_3	0.3095	9.4907
	"	CrO_4	0.3594	9.5556
	$BaCrO_4$	Cr	0.2052	9.3125
	"	CrO_3	0.3947	9.5963
	"	CrO_4	0.4580	9.6609
Cobalt	Co	CoO	1.2713	0.1043
	$CoSO_4$	Co	0.3804	9.5802
	"	CoO	0.4835	9.6844

*The −10 after the logarithms is omitted.

CHEMICAL FACTORS AND THEIR LOGARITHMS—*Continued*

	Weighed.	Required.	Factor.	Log.*
Copper	Cu	CuO	1.2517	0.0975
	CuO	Cu	0.7989	9.9025
	Cu_2S	Cu	0.7986	9.9023
	"	CuO	0.9996	9.9998
	$Cu_2(CNS)_2$	Cu	0.5226	9.7181
Fluorine	CaF_2	F	0.4866	9.6872
Hydrogen	H_2O	H	0.1119	9.0488
Iodine	AgI	I	0.5405	9.7328
	"	HI	0.5448	9.7362
Iron	Fe_2O_3	Fe	0.6994	9.8447
	"	FeO	0.8998	9.9542
Lead	PbO	Pb	0.9283	9.9677
	PbO_2	Pb	0.8662	9.9376
	PbS	Pb	0.8659	9.9375
	"	PbO	0.9328	9.9698
	$PbSO_4$	Pb	0.6831	9.8345
	"	PbO	0.7359	9.8668
	$PbCl_2$	Pb	0.7449	9.8721
	"	PbO	0.8025	9.9044
	$PbCrO_4$	Pb	0.6410	9.8068
	"	PbO	0.6905	9.8392
Magnesium	MgO	Mg	0.6032	9.7804
	$Mg_2P_2O_7$	Mg	0.2184	9.3392
	"	MgO	0.3621	9.5588
	$MgSO_4$	Mg	0.2020	9.3054
	"	MgO	0.3349	9.5249
Manganese	Mn_3O_4	Mn	0.7203	9.8575
	"	MnO	0.9301	9.9685
	MnS	Mn	0.6314	9.8003
	"	MnO	0.8153	9.9113
	$Mn_2P_2O_7$	Mn	0.3867	9.5874
	"	MnO	0.4996	9.6986
	$MnSO_4$	Mn	0.3638	9.5608
	"	MnO	0.4697	9.6718
Mercury	Hg	HgO	1.0800	0.0334
	HgS	Hg	0.8622	9.9356
	"	HgO	0.9308	9.9689
	HgCl	Hg	0.8498	9.9293
	"	HgO	0.9174	9.9626
Molybdenum	MoO_3	Mo	0.6667	9.8239
Nickel	Ni	NiO	1.2727	0.1047
	NiO	Ni	0.7858	9.8953
	$NiSO_4$	Ni	0.3793	9.5790
	"	NiO	0.4827	9.6837

* The −10 after the logarithms is omitted.

CHEMICAL FACTORS AND THEIR LOGARITHMS—*Continued.*

	Weighed.	Required.	Factor.	Log.*
Nitrogen	$(NH_4)_2PtCl_6$	N	0.0631	8.8000
	"	NH_3	0.0767	8.8848
	"	NH_4	0.0812	8.9098
	Pt	N	0.1435	9.1570
	"	NH_3	0.1745	9.2418
	"	NH_4	0.1848	9.2678
Phosphorus	$Mg_2P_2O_7$	P	0.2787	9.4452
	"	PO_4	0.8534	9.9312
	"	P_2O_5	0.6379	9.8048
	$(NH_4)_3PO_4.12MoO_3$	P	0.0165	8.2185
	"	PO_4	0.0506	8.7044
	"	P_2O_5	0.0378	8.5780
Potassium	KCl	K	0.5244	9.7197
	"	K_2O	0.6317	9.8005
	K_2PtCl_6	K	0.1608	9.2064
	"	K_2O	0.1938	9.2873
	K_2SO_4	K	0.4487	9.6520
	"	K_2O	0.5405	9.7328
Selenium	Se	SeO_2	1.4040	0.1474
Silicon	SiO_2	Si	0.4693	9.6715
Silver	AgCl	Ag	0.7526	9.8766
	AgBr	Ag	0.5744	9.7592
	AgI	Ag	0.4595	9.6622
	Ag_2S	Ag	0.8707	9.9399
Sodium	NaCl	Na	0.3934	9.5949
	"	Na_2O	0.5303	9.7245
	Na_2SO_4	Na	0.3238	9.5103
	"	Na_2O	0.4364	9.6399
	Na_2CO_3	Na	0.4345	9.6380
	"	Na_2O	0.5853	9.7674
Strontium	$SrCO_3$	Sr	0.5936	9.7735
	"	SrO	0.5641	9.8463
	$SrSO_4$	Sr	0.4770	9.6785
	"	SrO	0.5641	9.7514
Sulphur	$BaSO_4$	S	0.1374	9.1379
	"	SO_2	0.2745	9.4385
	"	SO_3	0.3430	9.5353
	"	SO_4	0.4115	9.6144
	"	H_2SO_4	0.4202	9.6234
Tin	SnO_2	Sn	0.7881	9.8966
Titanium	TiO_2	Ti	0.6005	9.7785
Uranium	$(UO_2)_2P_2O_7$	U	0.6670	9.8241
	"	U_3O_8	0.7877	9.8964
	U_3O_8	U	0.8482	9.9285
Zinc	ZnO	Zn	0.8034	9.9049
	ZnS	Zn	0.6709	9.8266
	"	ZnO	0.8351	9.9217

* The −10 after the logarithms is omitted.

LOGARITHMS

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

Logarithms.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS

Logarithms.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3556	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9944	9977	2	5	7	9	11	14	16	18	20

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